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Solid-phase microextraction based sampling techniques for the analysis of volatile organic compounds in the atmosphere

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ACADEMIC DISSERTATION

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Abstract

Volatile organic compounds (VOCs) comprise a large diversity of species that are emitted into the atmosphere from both biogenic and anthropogenic sources. These species play a key role in atmospheric photochemistry, due to their high reactivity with atmospheric oxidants, and in the formation and growth of secondary organic aerosols. The trace levels usually found in ambient air and the enormous heterogeneity of VOC sources and emissions around the Earth call for the development of novel analytical methodologies and portable devices, which provide reduced analytical steps and allow the measurement of these compounds at virtually any spatial location.

The main goal of this doctoral thesis was to develop further and apply solid-phase microextraction (SPME) based analytical methods for the sampling and analysis of VOCs in the atmosphere. The SPME techniques used included conventional SPME fibers, needle trap microextraction (NTME) devices and a novel SPME Arrow system. Portable gas chromatography-mass spectrometry (GC-MS) was employed for the fast on-site measurement of atmospheric volatiles. Field measurements were performed at the Station for Measuring Ecosystem-Atmosphere Relations (SMEAR II) in Hyytiälä, Finland.

Dynamic SPME collection combined with portable GC-MS allowed the rapid on-site measurement of the most abundant compounds present in the sampling site atmosphere with minimal analytical steps. The potential of NTME and portable GC-MS for the field measurement of biogenic and anthropogenic organic volatiles was also demonstrated, and the method developed was applied to clarify the effect of snow pack on the concentration of biogenic volatile organic compounds (BVOCs) in the air. SPME and portable GC-MS were used for the characterization of BVOCs emitted from chambers installed at the forest soil. A novel SPME Arrow system was also successfully characterized and employed for the sampling of atmospheric VOCs.

The results demonstrated the great potential and versatility of SPME-based sampling techniques combined with portable GC-MS for the rapid on-site sampling and analysis of VOCs in the atmosphere.

Preface

This thesis is based on research carried out at the Department of Chemistry, University of Helsinki, during the years 2013-2017. Financial support was provided by the Academy of Finland Center of Excellence programme (grant no. 307331) and the Doctoral Programme in Atmospheric Sciences.

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List of original publications

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I. **Barreira, L.M.F.,** Parshintsev, J., Karkkainen, N., Hartonen, K., Jussila, M., Kajos, M., Kulmala, M., Riekkola, M-L., Field measurements of biogenic volatile organic compounds in the atmosphere by dynamic solid-phase microextraction and portable gas chromatography-mass spectrometry, *Atmospheric Environment*, 115, 214-222 (2015), doi: http://dx.doi.org/10.1016/j.atmosenv.2015.05.064
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II. **Barreira, L.M.F.,** Xue, Y., Duporte, G., Parshintsev, J., Hartonen, K., Jussila, M., Kulmala, M., Riekkola, M-L., Potential of needle trap microextraction-portable gas chromatography-mass spectrometry for measurement of atmospheric volatile compounds, *Atmospheric Measurement Techniques*, 9, 3661-3671 (2016), doi: http://dx.doi.org/10.5194/amt-9-3661-2016
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III. **Barreira, L.M.F.,** Duporte, G., Parshintsev, J., Hartonen, K., Jussila, M., Aalto, J., Back, J., Kulmala, M., Riekkola, M.-L., Emissions of biogenic volatile organic compounds from the boreal forest floor and understory: a study by solid-phase microextraction and portable gas chromatography-mass spectrometry, *Boreal Environment Research*, 22, 393-413 (2017).
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IV. **Barreira, L.M.F.**, Duporte, G., Rönkkö, T., Parshintsev, J., Hartonen, K., Schulman, L., Heikkinen, E. Jussila, M., Kulmala, M., Riekkola, M.-L., Field measurements of biogenic volatile organic compounds in the atmosphere using solid-phase microextraction ARROW*, Published as a discussion paper in Atmospheric Measurement Techniques Discussions,*
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The contribution of the author:
Analysis of data obtained from field measurements (Paper I); experimental work related to sample collection, sample preparation, chromatography, mass spectrometry and data analysis (Papers II–IV); main responsibility for writing the manuscript (Papers I–IV).

Publications not included in the thesis:

Duporte, G., Riva, M., Parshintsev, J., Heikkinen, E., **Barreira, L.,** Myllys, N., Heikkinen, L., Hartonen, K., Kulmala, M., Ehn, M., Riekkola, M.-L., Chemical Characterization of Gas- and Particle-Phase Products from the Ozonolysis of α-Pinene in the Presence of Dimethylamine, *Environmental Science and Technology*, 51, 5602-5610 (2017), doi: 10.1021/acs.est.6b06231.

Duporte, G., Parshintsev, J., **Barreira, L.M.F.,** Hartonen, K., Kulmala, M., Riekkola, M-L., Nitrogen-Containing Low Volatile Compounds from Pinonaldehyde-Dimethylamine Reaction in the Atmosphere: A Laboratory and Field Study, *Environmental Science and Technology*, 50, 4693-4700 (2016), doi: 10.1021/acs.est.6b00270.

List of Abbreviations

AVOCs	Anthropogenic volatile organic compounds
BTEX	Benzene, toluene, ethylbenzene and xylenes
BVOCs	Biogenic volatile organic compounds
CAR/PDMS	Carboxen/polydimethylsiloxane
CE	Capillary electrophoresis
CI	Chemical ionization
DMA	Dimethylamine
DMAPP	Dimethylallyl pyrophosphate
DVB/CAR/PDMS	Divinylbenzene/carboxen/polydimethylsiloxane
DXP	Deoxyxylulose-5-phosphate
EA	Ethylamine
EC	Eddy covariance
EI	Electron ionization
EIC	Extracted ion chromatogram
FAC	Field analytical chemistry
GC-MS	Gas chromatography-mass spectrometry
GPP	Geranyl pyrophosphate
IPP	Isopentenyl pyrophosphate
MVA	Mevalonic acid
NTD	Needle trap device
NTME	Needle trap microextraction
PA	Polyacrylate
PAN	Peroxyacyl nitrates
PAR	Photosynthetic active radiation
PBL	Planetary boundary layer
PDMS/DVB	Polydimethylsiloxane/divinylbenzene
PNC	Particle number concentration
ppbv	Parts per billion by volume
pptv	Parts per trillion by volume
PTR-MS	Proton-transfer-reaction mass spectrometry
SMEAR	Station for measuring ecosystem-atmosphere relations
SOA	Secondary organic aerosol
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
sVOCs	Semi-volatile organic compounds
TIC	Total ion chromatogram
VOCs	Volatile organic compounds

List of Symbols

a_R	Constant that depends on the volumes of extraction phase, headspace and sample, mass transfer constants, distribution coefficients and the surface are of extraction phase [s^{-1}]
C_o	Initial concentration in the sample [M]
C_A^0	Initial concentration of analyte A in the sample [M]
C_e^∞	Concentration in the extraction phase at equilibrium [M]
C_f^∞	Equilibrium concentration of analyte on the fiber [M]
C_{fA}^∞	Equilibrium concentration of analyte A on the fiber in the presence of a competing compound B [M]
C_{fmax}	Maximum concentration of active sites on the coating [M]
C_s^0	Initial concentration of analyte in the sample [M]
C_s^∞	Sample concentration at equilibrium [M]
C_{sB}^∞	Equilibrium concentration of analyte B in the sample [M]
K	Analyte´s adsorption equilibrium constant
K_A	Adsorption equilibrium constants for compound A
K_B	Adsorption equilibrium constants for compound B
K_{fs}	Distribution coefficient of the analyte between the fiber coating and sample matrix
n_o	Amount of analyte initially present in the sample [mol]
n_1, n_2, … ,	Amount of analyte present in the discontinuous phases [mol]
n	Amount of extracted analyte [mol]
n_e	Amount of analyte present in the extraction phase [mol]
n_s	Amount of analyte present in the homogeneous liquid phase [mol]
t	Sampling time [s]
T	Temperature [K]
V_e	Volume of extraction phase [L]
V_f	Fiber coating volume [L]
V_s	Sample volume [L]

1 Introduction

Volatile organic compounds (VOCs) are ubiquitous constituents of Earth´s atmosphere. Their atmospheric presence is caused by production, emission and transport processes from both natural and anthropogenic origins, and most of these species can reach mixing ratios of some parts per trillion by volume (pptv) to parts per billion by volume (ppbv) [1]. On the global scale, biogenic sources contribute most to the VOC emissions, even though anthropogenic sources are often dominant within urban areas [1]. Due to the fast reaction rates with atmospheric oxidants, VOCs determine the oxidative photochemistry of troposphere [2, 3]. The oxidation products of these trace gases are also involved in secondary organic aerosol (SOA) formation and growth, which impact on atmospheric radiative processes by scattering and/or absorbing radiation and by acting as cloud condensation nuclei and ice nuclei [3, 4].

The measurement of VOCs in the atmosphere is often performed by using sampling tubes filled with an adsorbent material that are thermally desorbed into a gas chromatograph-mass spectrometer [5-7]. This method allows the *in-situ* measurement of VOCs with a reasonable time resolution [7]. Its main limitation is the requirement of sophisticated instrumentation that is less convenient for field measurements (e.g. thermodesorption unit and cryofocusing). More recently, proton-transfer-reaction mass spectrometry (PTR-MS) has been also employed for long term *in-situ* measurements of trace levels of VOCs, mainly due to its high sensitivity, ability to monitor concentration changes over small time intervals and capability to perform flux measurements [8, 9]. However, separation of compounds with the same molecular mass is not feasible.

The focus of this work was to develop novel SPME-based sampling methods for the analysis of VOCs in the atmosphere. SPME is a sampling technique that was developed to address the need for rapid sample preparation both in laboratory and on-site [10]. The principle of this technique consists in the exposure of micro quantities of solid sorbent or liquid polymers in an appropriate format to the sampling media, and its inherent characteristics permit to combine sampling, isolation and enrichment in a single analytical step [11]. Recent advances related to the use of SPME include the development of new coatings, derivatization techniques and formats of sampling devices [12].

The sampling techniques used in this thesis included conventional SPME fibers, needle trap microextraction (NTME) devices and a novel SPME Arrow sampling system. SPME was combined with conventional and portable GC-MS that allowed fast on-site analysis of the most abundant VOCs at the boreal forest site.

The specific aims of the study were the following:

- To develop a new methodology involving dynamic SPME sampling and portable GC-MS for the analysis of BVOCs in atmosphere (Paper I).
- To evaluate the potential of NTME sampling combined with portable GC-MS for the on-site measurement of atmospheric volatile compounds (Paper II).
- To collect air samples directly from soil chambers by SPME for the clarification of understory emissions measured by portable GC-MS (Paper III).
- To study the performance of a novel SPME Arrow system for the collection of BVOCs from ambient air (Paper IV).

2 Background to the work

2.1 Volatile organic compounds

Earth is a complex and partially self-regulated system, consisting of interlinked physical, chemical and biological components [13]. Chemical elements within biogeochemical cycles flow in various forms between biotic and abiotic components of Earth´s ecosystems. All living organisms produce volatile organic compounds (VOCs), such as hydrocarbons, consisting solely of hydrogen and carbon, or other VOCs containing elements such as oxygen, nitrogen or sulfur [14].

According to the European Directive 2008/50/EC (European Parliament and Council 2008), VOCs are defined as "organic compounds from anthropogenic and biogenic sources, other than methane, that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight" (European Environmental Agency, 2013).

These ubiquitous volatile compounds are emitted into the atmosphere from anthropogenic (e.g. vehicular exhaust and industrial emissions) and biogenic sources (e.g. forest vegetation and soil). On a global scale, biogenic volatile organic compounds (BVOCs) are roughly one order of magnitude larger than the anthropogenic counterpart [2, 3]. Even though anthropogenic volatile organic compounds (AVOCs) constitute a small fraction of the total VOCs, they greatly dominate in urban and industrial areas and in remote areas when biomass burning occurs [14].

BVOCs are a very heterogeneous group of compounds, which include the isoprenoids (isoprene and monoterpenes), alkanes, alkenes, carbonyls, alcohols, esters, ethers, acids and others [15]. This large variety of organic molecules has inherent differences in sizes, physicochemical properties and metabolic origin [16]. Some BVOCs are largely lipophilic, and due to their high vapor pressures they are released into the atmospheric air in significant amounts [17]. Globally, isoprenoids are the most prominent chemical group of compounds emitted into the atmosphere, followed by alcohols and carbonyls [15].

Once in the atmosphere, BVOCs take part in several natural processes, including plant defense and communication [13, 16]. In addition to their biological impacts, they influence the local and regional atmospheric photochemistry. BVOCs, and particularly their unsaturated fraction, are highly reactive with atmospheric oxidants such as ozone (O_3), hydroxyl radicals (OH) and nitrate radicals (NO_3) [18]. Therefore, BVOCs play an important role in determining the oxidative capacity of the atmosphere. Some of the resulting less volatile photo-oxidation products will also partition between the gas and particle phase and promote the formation and growth of atmospheric aerosols [19]. Aerosols have an impact on Earth´s climate, both directly by reflecting or absorbing solar radiation and/or indirectly by acting as cloud condensation nuclei [20].

2.1.1 Monoterpenes

Monoterpenes represent the dominant class of BVOCs emitted by coniferous forests [21]. The biosynthesis of monoterpenes occurs predominantly through the deoxyxylulose-5-phosphate (DXP) pathway in the plastids, preferably in leucoplasts, and involves a combination of two units of five carbon intermediates (C5), isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP) [15, 22, 23]. The resulting ten-carbon (C10) precursor, geranyl pyrophosphate (GPP), is the starting unit for the production of monoterpenes based on the activities of different enzymes (e.g. monoterpene cyclases) [15, 24].

The produced monoterpenes are then stored in specialized plant organs, such as resin ducts or glandular trichomes, and are further released to operate a variety of natural functions that include defense against predators and communication between species [25, 26]. Monoterpene pool emissions are temperature dependent, according to the vapor pressure and transport resistance along the diffusion path, and are generally regarded as light-independent [15]. However, substantial *de novo* emissions were also found in more recent studies [27]. Mixing ratios of monoterpenes are generally higher during the night time due to the lower amounts of atmospheric oxidants, the absence of light and their accumulation in a shallower nocturnal boundary layer [28, 29].

Each plant species synthesizes a unique set of volatiles [30]. Numerous terpenoids containing a combination of the C_5 isoprenoid structure can be produced, and up to 5000 different terpenoid structures have been identified in emissions from vegetation [29]. An intrinsic characteristic of monoterpenes is the presence of one or more double bonds in their structure (Fig. 1). These double bonds can be present inside and/or outside the ring structure, or in acyclic monoterpene structures [29].

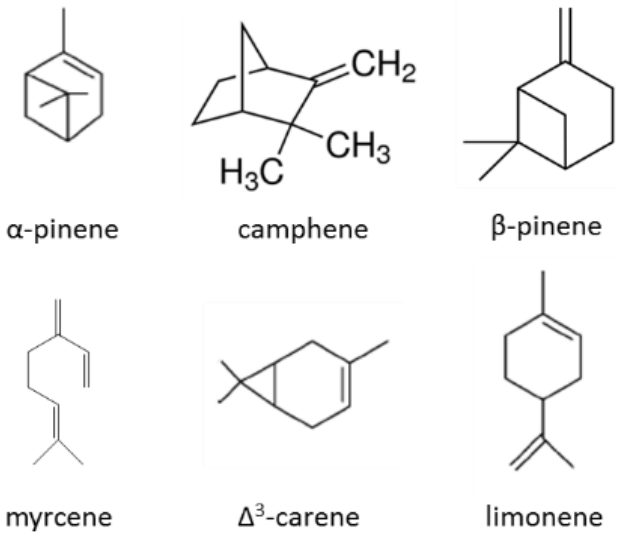

Figure 1. *Chemical structures of selected terpenoid compounds.*

As a consequence of the structural diversity and singularity concerning the double bond position, monoterpenes have a very distinct reactivity with atmospheric oxidants and consequently their lifetimes vary considerably between different species [31]. The oxidation products formed (Fig. 2) depend on the monoterpene species involved in atmospheric photochemical reactions and have a major impact on the global SOA burden [31, 32].

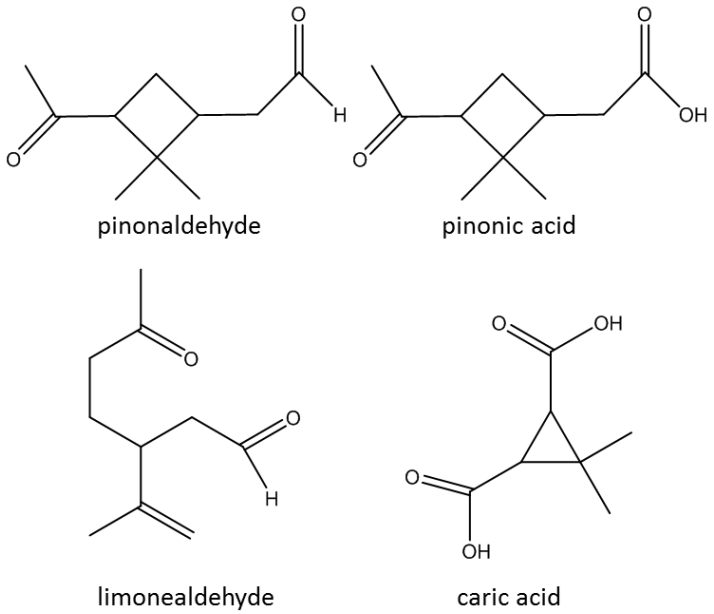

Figure 2. *Chemical structures of selected monoterpene oxidation products.*

2.1.2 Carbonyl compounds

Carbonyl compounds, including aliphatic aldehydes, also play an important role in atmospheric chemistry and physics. These compounds are known to participate in photochemical reactions that condition the oxidative capacity of atmosphere, e.g. by formation of tropospheric ozone and peroxyacyl nitrates (PAN) [15]. Heterogeneous reactions of aldehydes in the presence of an acidic catalyst, such as sulfuric acid (H_2SO_4), also generate a marked increase in organic aerosol yield, adding to SOA formation and growth [15, 33].

The main contributions to the atmospheric budget of carbonyls arise from secondary reactions of biogenic and anthropogenic hydrocarbons with atmospheric oxidants (OH, O_3, NO_3) and photolysis [15]. However, the primary production of biogenic carbonyls also occurs. In particular, saturated C_6-C_{10} aldehydes have been measured in enclosure studies where plants were exposed to ozone [34]. In the same study, the emission patters of measured aldehydes were dependent on temperature and emissions were also generated

when plants were exposed to pathogen and insect attack. Primary anthropogenic sources have been also reported, including emissions from biomass burning, vehicular exhaust, food cooking and indoor sources (e.g. cigarette smoke, cleaning agents, or paints) [35-38].

A diversity of carbonyl compounds (C_1-C_{12}) have been measured during several field campaigns performed at different locations, including at the boreal coniferous forest in Hyytiälä, Southern Finland [29, 39]. The lifetimes of carbonyls at this particular ecosystem have been also calculated, and for the most of the compounds the main sink during spring season was caused by their atmospheric reaction with OH radicals and photolysis [39]. However, these compounds have lifetimes greater than the ones observed for monoterpenes due to the lack of a double bond in their structure. Their contribution to atmospheric photochemistry and secondary aerosols is then expected to be smaller when compared to the more reactive terpenoid compounds.

2.1.3 Aromatic hydrocarbons

Aromatic VOCs are atmospheric pollutants that are commonly present in the urban and regional atmosphere [40, 41]. Some compounds, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) (Fig. 3), have attracted attention due to the concerns associated to their ozone formation potentials and nefarious human health implications [42-44]. The predominant sources of these compounds are associated to fossil fuel evaporation and combustion, industrial processes and solvent use [1].

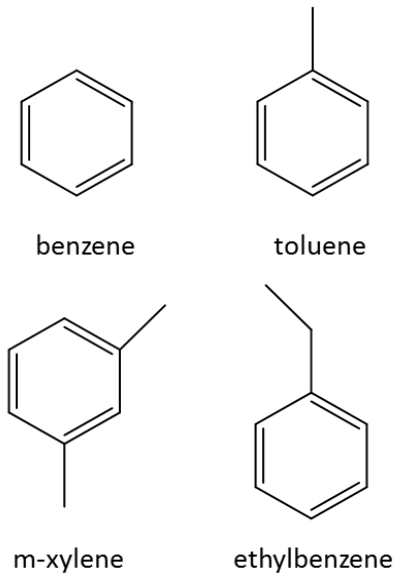

Figure 3. *Chemical structures of selected aromatic hydrocarbons.*

Diurnal and seasonal variations of aromatic hydrocarbons have been reported. Diurnal variations display concentration peaks in traffic rush hours, indicating the effect of traffic volume [45]. Seasonal variations are characterized by higher concentrations during winter and lower concentrations during summer [42]. Larger evaporative emissions are found in summer while vehicular emissions are generally higher during winter [42]. The increase of evaporative emissions in summer is mainly related to the higher temperature in this period of the year, while the higher concentrations in winter are a combination of higher emissions from fossil-fuel vehicles and a lower chemical reactivity of atmosphere in the cold season [29].

Anthropogenic VOCs can also be found at remote regions, such as forest ecosystems. Higher concentrations of these compounds are usually observed due to long range transport of air masses from polluted areas or after forest fire events [46-48]. This fact is directly related with their relatively long lifetimes in the atmosphere [49]. These anthropogenic tracers have also been measured at the boreal forest of Hyytiälä, in Finland, and BTEXs were the most abundant aromatic AVOCs [50, 51].

2.2 Solid-phase microextraction based sampling techniques

Solid-phase microextraction (SPME) is a sampling technique that was developed by Pawliszyn in 1989, to address the need for rapid sample preparation both in laboratory and on-site [10, 52]. The first SPME fibers become commercially available in 1993, and since then this methodology has been continuously developed [53, 54]. The most common applications are in the field of organic compounds, mostly VOCs, and are limited by the properties of commercially available extraction phase materials [53]. A diversity of SPME sorbent coatings are available today, including polydimethylsiloxane/divinylbenzene (PDMS/DVB), polyacrylate (PA), carboxen/polydimethylsiloxane (CAR/PDMS) and DVB/CAR/PDMS.

SPME combines sampling, extraction and pre-concentration into a one single step, eliminating the need for solvents or complicated apparatus and reducing the time required for sample preparation [55]. SPME devices are particularly attractive for field measurements due to their simplicity, solventless operation, portability, reusability, high enrichment properties, compatibility with commonly used instrumentation and minimum impact on the sampled system by the collection of a small fraction of total target analyte [56].

Due to these inherent characteristics, SPME copes with several principles that are mandatory for practicing a Green Analytical Chemistry [57]. Several configurations of SPME have been developed to address the issues associated with its implementation [10]. These include coated fibers, vessels, agitation mechanism disks and in-tube approaches such as needle-trap microextraction [10]. In comparison with conventionally used adsorbent tubes, SPME is more convenient since it does not require the installation of additional

instrumentation that is critical for thermal desorption-GC-MS instruments (e.g. desorption unit and cold trap). However, particularly for equilibrium-based sampling, quantitation is also more challenging due to the diversity of factors influencing analyte collection.

2.2.1 Solid-phase microextraction

In SPME, micro quantities of solid sorbent or liquid polymer are exposed to the sample for a well-defined period of time [58]. The sampling with conventional SPME fibers (Fig. 4) consists of the partition of analytes between the extraction phase and the sample matrix, and subsequent desorption of concentrated extracts into the analytical instrument [54]. SPME has mostly been used in combination with gas chromatography-mass spectrometry (GC-MS), even though other applications involving liquid chromatography-mass spectrometry (HPLC-MS), capillary electrophoresis (CE) and many other techniques have been also reported [54, 59].

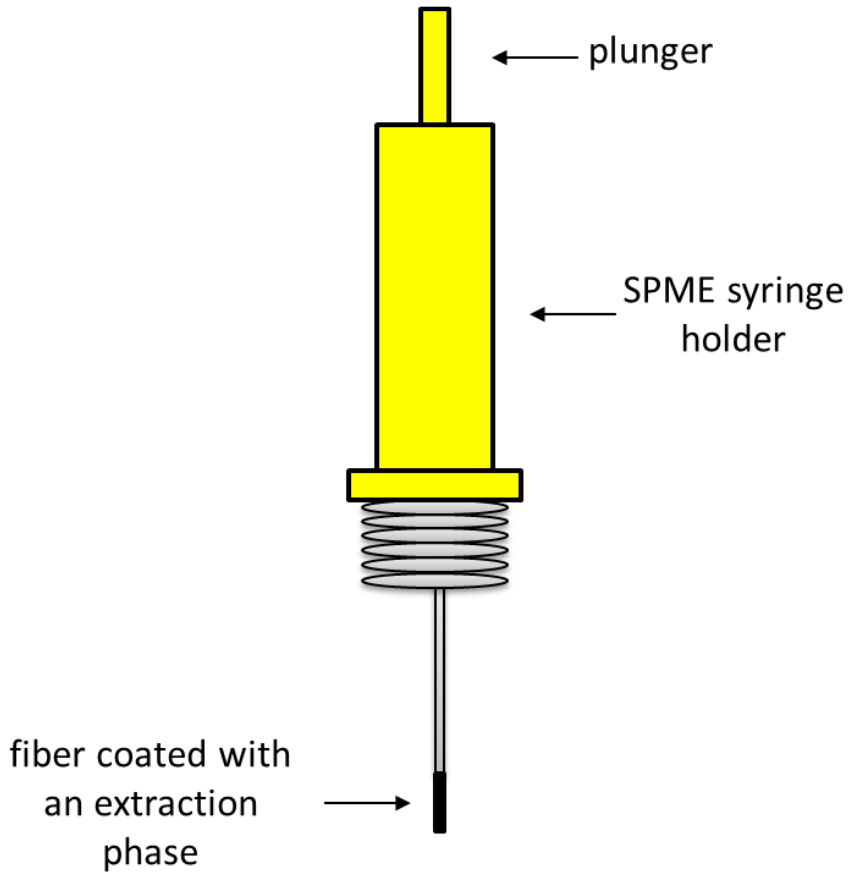

Figure 4. *Commercial SPME syringe device.*

When liquid-polymer based coatings are used, analytes dissolve within the sorbent while with solid sorbents extraction occurs only at the surface of the coating within the experimental time [60]. Therefore, extraction kinetics are faster for adsorbent-based fibers. However, adsorbent fibers have also a smaller linear dynamic range and suffer from displacement and carry-over effects [60]. Two different approaches can be used for the sampling of analytes by SPME, which consist of equilibrium and pre-equilibrium extraction.

In the equilibrium extraction approach, a partition equilibrium between the sample matrix and extraction phase is reached and the amount of analytes extracted is consequently not affected by the convection conditions and collection time [60]. When immobilized liquid fibers are used, the sampling process is analogous to liquid-liquid extraction. Consequently, by the law of conservation of mass, the initial amount of analyte present in the sample will be equal to the sum of the individual amounts of analyte present in all the discontinuous phases:

$$n_0 = n_e + n_s + n_1 + n_2 + \cdots, \tag{1}$$

where n_0 *is* the amount of analyte initially present in the natural sample, n_e is the amount of analyte in the extraction phase, n_s is the amount of analyte in the homogeneous liquid phase and $n_1 + n_2 + \cdots$, are the amounts of analyte in the discontinuous phases [60].

When the phases that contribute significantly to the extraction process are only the sample matrix and the extraction phase, the amount of analyte extracted by the fiber is then described as:

$$n_0 = n_e + n_s \Leftrightarrow C_o V_s = C_e^{\infty} V_e + C_s^{\infty} V_s, \tag{2}$$

where C_o is the initial concentration in the sample, V_s is the sample volume, C_s^{∞} is the sample concentration at equilibrium, C_e^{∞} is the concentration in the extraction phase at equilibrium and V_e is the volume of extraction phase [60].

On the other hand, when solid sorbent fibers are used, analytes bind to surface active sites and the equilibrium amount of analyte is determined by:

$$n_f^{\infty} = C_f^{\infty} V_f = \frac{K C_s^0 V_s V_f \left(C_{fmax} - C_f^{\infty}\right)}{V_s + K V_f \left(C_{fmax} - C_f^{\infty}\right)}, \tag{3}$$

where C_f^{∞} is the equilibrium concentration of analyte on the fiber, V_f is the fiber coating volume, K is the analyte´s adsorption equilibrium constant, C_s^0 is the initial concentration of analyte in the sample and C_{fmax} is the maximum concentration of active sites on the coating [60].

The amount of analyte A extracted at equilibrium is, however, affected by the presence of a competing compound B, and under these conditions is given by the following equation:

$$n_{fA}^{\infty} = C_{fA}^{\infty} V_f = \frac{C_A^0 V_s V_f K_A \left(C_{fmax} - C_{fA}^{\infty}\right)}{(1 + K_B C_{sB}^{\infty}) V_s + K_A V_f \left(C_{fmax} - C_{fA}^{\infty}\right)}, \quad (4)$$

where C_{fA}^{∞} is the equilibrium concentration of analyte A on the fiber in the presence of a competing compound B, C_A^0 is the initial concentration of analyte A in the sample, K_A and K_B are the adsorption equilibrium constants for compound A and B respectively and C_{sB}^{∞} is the equilibrium concentration of analyte B in the sample [60].

The other possible approach involves the use of a short-time pre-equilibrium extraction, and if convection or agitation are kept constant the amount of analytes extracted is related to time [60]. The entire kinetic process of SPME can be described by:

$$n = [1 - \exp(-a_R t)] \frac{K_{fs} V_f V_s}{K_{fs} V_f + V_s} C_O , \quad (5)$$

where n is the amount of extracted analyte at time t, K_{fs} is the distribution coefficient of analyte between the fiber coating and sample matrix and a_R is a constant that depends on the volume of extraction phase, headspace and sample volumes, mass transfer constants, distribution coefficients and the surface of extraction phase [60, 61].

Several extraction parameters affect the collection efficiencies when using SPME, requiring careful optimization of the method prior to practical application of the technique. The adsorption of analyte onto the SPME sorbent is an exothermic process and increasing temperature will reduce the distribution constant of analytes [55]. Adjustment of sample pH can improve the extraction efficiency for basic and acid analytes [60]. Salt addition increases the ionic strength of the sample solution, which improves sensitivity in many applications by causing a salting-out effect for polar analytes whose solubility decreases in the presence of large amounts of salts [56]. The sensitivity of SPME is proportional to the number of molecules extracted from the sample and, when sample volume increases, the amount of analyte extracted also increases until the volume of sample becomes significantly larger than the volume of fiber and the distribution coefficient [60]. Relative humidity can decrease the amount of analyte extracted [62]. Furthermore, the presence of organic solvent can cause swelling of the fiber, which will cause recovery and precision problems [56].

2.2.2 Solid-phase microextraction Arrow

Solid phase microextraction Arrow (Fig. 5) is a new SPME system that consists of a steel rod coated with a larger volume of sorbent material than conventional SPME fibers [63]. This device was recently patented by Schueler and Schillig [64] and has been already successfully used in a few research studies [63, 65].

SPME Arrow was developed to address the requirement of higher sorbent volume in SPME for improving detection limits without the need of modifications on the injection port of conventional GC-MS instruments, such as the installation of a desorption unit [63]. Indeed, due to its shape and dimensions, this device offers increased capacity, maintaining the compatibility for direct thermal desorption in the most commonly used injection ports of GC-MS [63]. The coated rod can also be withdrawn inside a steel tube, which improves the robustness of the device [63]. Due to its attractive characteristics and referred advantages, several additional applications are expected in numerous fields of research in the near future.

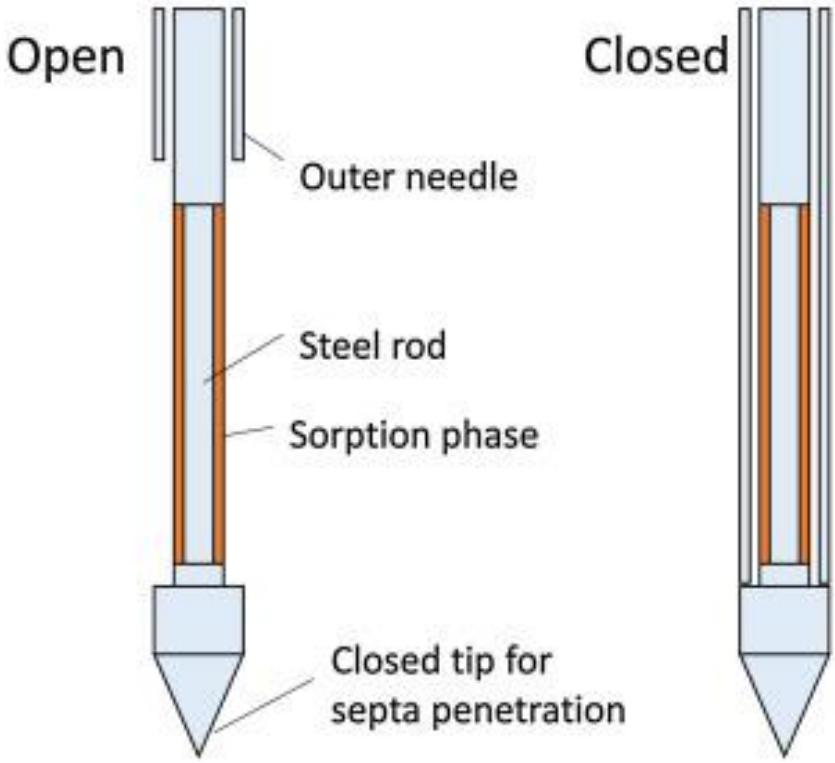

Figure 5. *The SPME Arrow system with sorbent exposed (left) and with sorbent covered by a steel tube (right). Reproduced from Elsevier [63].*

2.2.3 Needle trap microextraction

Other SPME-based configurations, operating in similar principles as SPME but with different concepts, are also commercially available. For instance, needle trap microextraction devices (NTD) (Fig. 6) consist of one or more sorbents immobilized inside the needle of the sampling device [66].

The main difference between this technique and SPME is its exhaustive extraction nature [67]. In NTME, quantitation is performed by determining the amount of compound exhaustively extracted by reference to instrument detector response calibration and expressing this amount per volume of sample [67]. This configuration also results in a more robust device, because sorbents are protected inside the needle, and allow to enhance capacity by increasing the sorbent length [68]. NTME can work effectively when used simultaneously with SPME, since NTME measures the total amount of analytes in the sample and SPME allows to concentrate free analytes with an associated selectivity provided by the coating material.

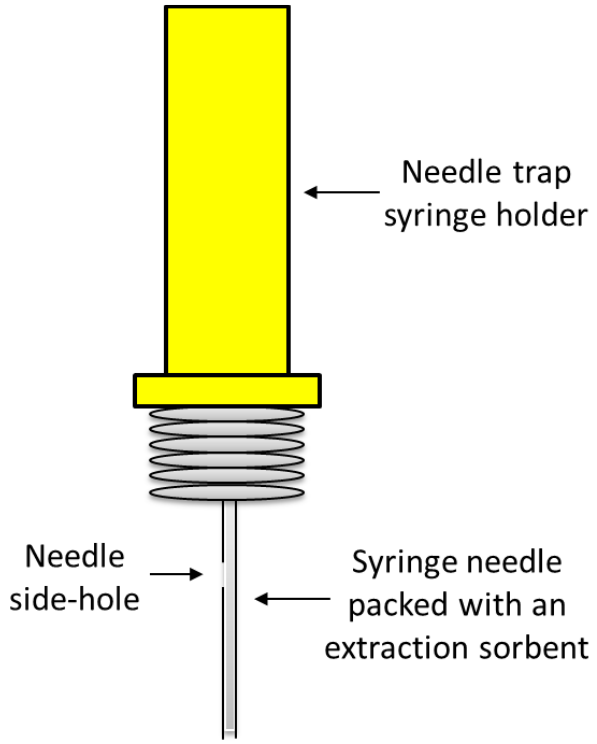

Figure 6. *Commercial NTME syringe device.*

However, NTME has also some drawbacks when compared to other conventional sampling techniques. The main disadvantage of NTME is a relatively small sample capacity, which restricts the volume of sample that can be collected. In addition, the desorption

temperature is limited by the temperature of the gas chromatographic injection port [69]. The capacity, described by the breakthrough volume of the needle trap, is also influenced by many factors, including concentration and composition, temperature, humidity, interferences, flow rate and sorbent bed geometry [70].

2.3 Field measurement of volatile organic compounds in the atmosphere

The growing global concerns about environmental sustainability, which have been chiefly triggered by the impacts caused by atmospheric pollutants on climate and human health, have encouraged the development of novel analytical methods for the determination of VOCs in the atmosphere. Atmospheric measurement of VOCs is burdensome, particularly due to the enormous diversity of VOC species, their different sources and reactivity, temporal and spatial variations of atmospheric emissions and concentrations, the very low mixing ratios of compounds to be analyzed and inconstancy of atmospheric parameters influencing VOC amounts in air, such as temperature, light, wind speed and wind direction [13, 15, 31, 71]. Several techniques and methodologies have been applied for the measurement of VOCs in the atmosphere, and the ones used in this work will be discussed in the following sections.

2.3.1 Gas chromatography-mass spectrometry

GC-MS is an analytical technique comprising the combination of a gas chromatograph coupled to a mass spectrometer (Fig. 7). This technique was developed in the mid-1950's, and has become a valuable tool in many different fields for the qualitative and quantitative determination of VOCs [72].

In brief, the sample is injected into the GC inlet, where it is vaporized and swept onto a chromatographic column (stationary phase) by the carrier gas (mobile phase). The chromatographic separation is based on the analyte distribution between these two phases and is effected by the choice of the stationary phase and the temperature of operation. The analytes are subsequently directed through a heated transfer line to the ion source, where they are converted to ions.

Two different methods are frequently used for ion production, the electron ionization (EI) and chemical ionization (CI). In EI, an electron beam of about 70 eV energy is impacted with the sample molecules. This high energy of the electrons is transferred to the analyte molecules, leading to their ionization and further fragmentation into smaller ions to release the excess of energy. The obtained fragmentation patterns can give valuable information about the structure of the analyte, but the extensive fragmentation of the molecule can also lead to the absence of the molecular ion from the obtained mass spectrum that may complicate a proper analyte identification. On the other hand, CI is based on the production

of ions by using a reagent gas initially ionized by an electron beam. In the most important CI ionization mechanism, the ionized reagent gas will subsequently transfer protons to/from the sample analytes and form a pseudo-molecular ion ($[M+H]^+$ or $[M+H]^-$). This softer ionization technique produces less fragmentation than EI and facilitates analyte identification by the presence of the molecular ion.

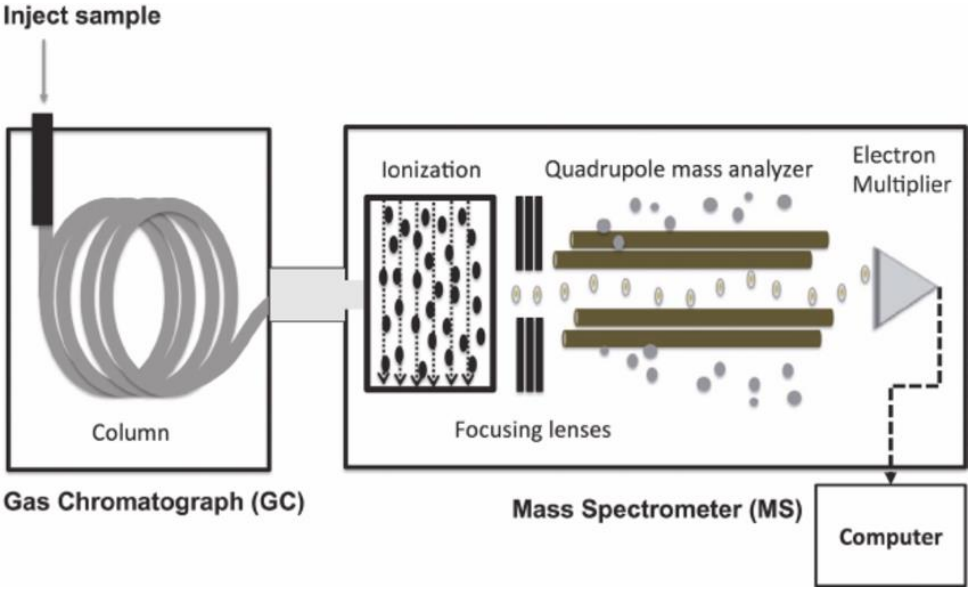

Figure 7. *Schematic diagram of a gas chromatograph-mass spectrometer (GC-MS). Open accessed from Nature Publishing Group [73].*

Ions are then accelerated to the mass analyzer, where they are separated according to their mass-to-charge (m/z) ratio. The most commonly used mass analyzer over the years is the quadruple mass spectrometer, mainly due to its small size, relatively low cost and ease of automation [74]. In this analyzer, mass separation occurs as a result of ion motion in a dynamic electric field and is dependent on the m/z of the ion [74]. Only ions of a single mass-to-charge ratio have stable trajectories, while all others are unstable in the x-and/or y-directions and hence lost from the two-dimensional trapping field [75].

2.3.2 Portable gas chromatography-mass spectrometry

Field analytical chemistry (FAC) is a rapidly growing area of chemical analysis in which the desired measurements are completely performed at the site of concern [76]. Traditional field sampling followed by laboratory analysis requires sample storage and transportation, which can cause sample alteration, a delay in the data availability and an increase in the overall price per sample [76]. Field analysis minimizes the time between sample collection and instrumental analysis, reducing the problems related to sample contamination, losses and degradation during transportation and storage [77]. The need for fast screening,

environmental monitoring and real-time decisions is moving the field of analytical instrumentation toward portable, faster and more cost-effective instrumentation for the measurement of target analytes directly on the field [76, 77].

Portable gas chromatographs integrated with a suitable detector, such as MS, are gaining popularity as new solutions for environmental monitoring and analysis [78]. In addition to the general requirements for field measurements, a portable GC-MS system must meet certain criteria, including a robust analytical performance, low power usage, minimal consumables, small size, fast analysis and rapid turnaround time [79]. Furthermore, these instruments should be environmental friendly to promote the necessary transition towards green analytical chemistry.

A portable GC-MS system that meets these criteria is the TRIDION-9^{TM} portable GC-MS (Fig. 8), which was developed by Torion Technologies Incorporated (American Fork, Utah, USA; http://torion.com). It is marketed as the world´s smallest person-portable GC-MS [79]. According to the manufacturer, TRIDION-9^{TM} was designed for rapid screening of chemicals in the field, such as environmental volatiles and semi-volatiles (sVOCs), explosives, chemical threat and hazardous substances.

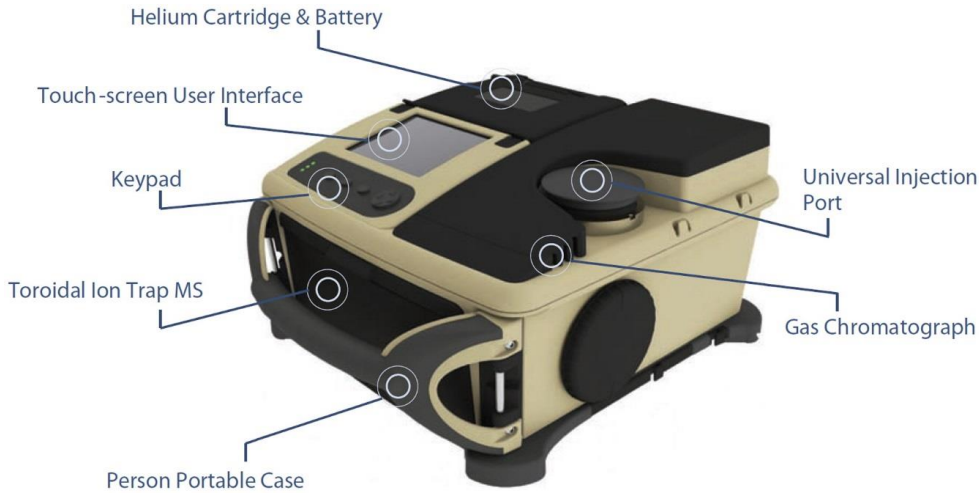

Figure 8. *The TRIDION-9 person-portable GC-MS. Reproduced from Taylor & Francis Group (http://www.tandfonline.com) [79].*

The instrument consists of a low thermal mass injector, a low thermal mass capillary gas chromatograph (containing a standard MXT-5 column, 5 m × 0.1 mm, 0.4 µm film thickness) with high-speed temperature programming, and a miniature toroidal ion trap mass analyzer with a mass spectral range of 41 to 500 Daltons. The weight of the instrument is 14.5 kg, and it can perform about 150 analysis, by using a 90 cm^3 high-purity helium carrier gas cylinder, and operate with a rechargeable lithium ion battery for up to 2.5 hours. This portable GC-MS is also considered reliable and easy to use.

An advantage of TRIDION-9™ when compared to conventional GC-MS instruments is its usability in the field without the need for additional electrical power, gas supply or equipment for data analysis [80]. The resistive heating provides a high heat efficiency, fast heating and allows to reduce the size of the column assembly by elimination of the oven, which makes low thermal mass GC ideal for fast analysis with minimum power consumption [80, 81]. Despite these advantages, resistive heating also has some limitations, including efficiency loss, complex manufacturing and inconvenient column maintenance [81].

Ion trap analyzers are ideal candidates for miniaturization when compared to other types of MS analyzers due to their inherent small size, simplicity, higher operating pressure that reduces vacuum requirements, less ion optic elements and capability to perform multiple stages of mass spectrometry (MS^n) in a single mass analyzer [82]. However, one limitation associated to miniaturizing ion traps is the reduction in ion storage capacity and consequent impact on sensitivity [82]. This limitation can be addressed by trapping ions in a toroidal geometry (Fig. 9), which maintains the unique advantages of conventional ion trap mass analyzers, such as the high pressure tolerance, small size and simplicity [82].

CUSTODION™ SPME fiber and needle trap microextraction syringes can be used in combination with TRIDION-9™. After sample collection, these SPME and NTME syringes are inserted directly into the heated injection port of the portable GC-MS, which will trigger the instrument to start a run automatically upon injection of the sample. SPME syringes contain a push-button trigger mechanism on the top that extends the fiber for sampling and sample injection or retracts the fiber inside the needle for its protection. Both SPME and NTME syringes contain also a screw-on/off cap for protection of collected analytes during transport and storage.

The recent progress in technology of field portable GC-MS instruments and the possibility of combination with SPME-based sampling techniques have increased their applications in environmental sample analysis. Examples of the diversity of these applications include their use for the qualitative identification of work-place air contaminants, study of differences in emission profiles of damaged and undamaged plant species, differentiation of volatile profiles from stockpiled almonds at different relative humidity levels, on-site analysis of ignitable liquid residues and field measurement of volatile organic compounds in the atmosphere [79, 83-86].

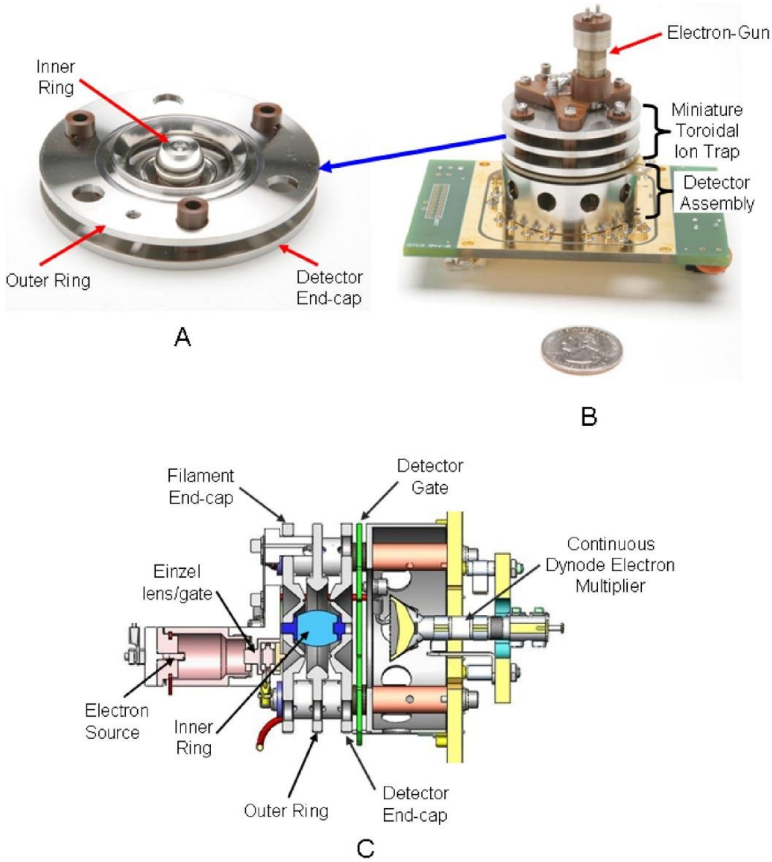

Figure 9. *Miniature toroidal ion trap mass spectrometer. (**a**) Photograph of ion trap electrodes with top end-cap removed to show the ion storage region. (**b**) Photograph of ion trap stack and detector board assembly. (**c**) Cross-sectional diagram of toroidal ion trap mass analyzer showing major components. The end of the GC column (not shown) is placed between the filament end-cap and outer ring of the toroidal ion trap assembly. Reproduced from Springer-Verlag [80].*

2.3.3 Proton-transfer-reaction mass spectrometry

In recent years, the field measurement of VOCs has been usually performed by online proton-transfer-reaction mass spectrometry (PTR-MS) [27, 87, 88]. PTR-MS was developed in the mid-1990's by the University of Innsbruck (Austria) [89]. Although not readily portable, it has been used in a range of field applications and inclusively deployed on research aircrafts and ships [8]. The instrument is constituted by four key components (Fig. 10): an ion source, a flow drift tube, a quadrupole mass analyzer and an ion detection system [8].

Briefly, reagent ions consisting of protonated water molecules (H_3O^+) are produced from pure water vapour at the ion source and mixed with the air sample inside the flow drift tube [90]. All volatile compounds with a proton affinity higher than water will eventually react with hydronium ions, according to the following reaction:

$$H_3O^+ + R \rightarrow H_2O + RH^+, \quad (6)$$

where R indicates the neutral volatile analyte [90]. The resulting products, which often suffer from low or no fragmentation, are then mass selected using a quadrupole mass analyzer and measured by count rates with an electron multiplier detector [8, 90].

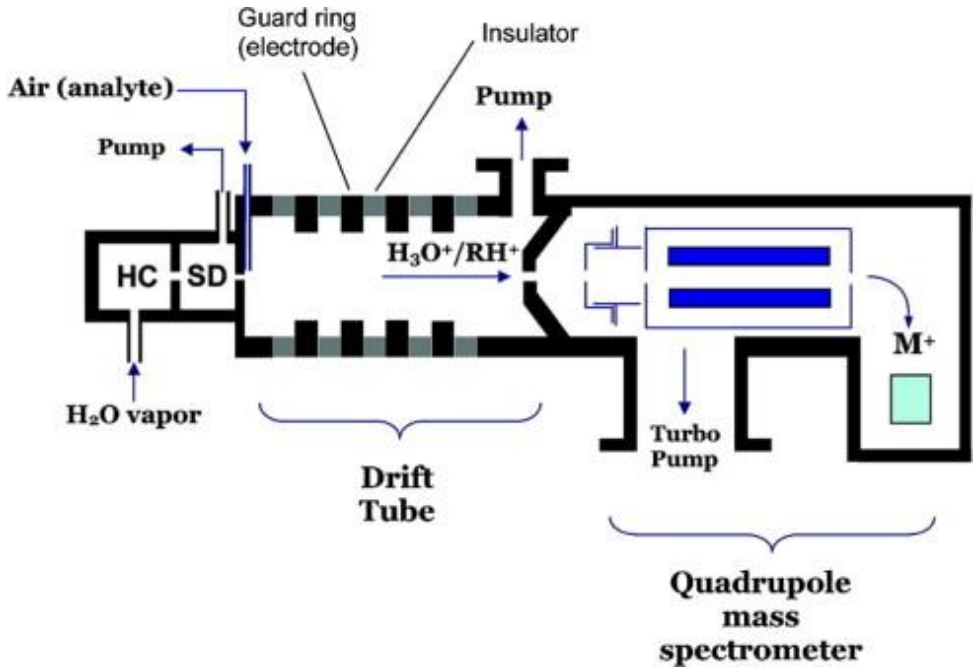

Figure 10. *Representation of a proton-transfer-reaction mass spectrometer. Reproduced from Elsevier [90].*

The main advantages of PTR-MS include real-time detection of VOCs with high sensitivity [91]. These characteristics are particularly suitable for measuring VOC emissions by Eddy Covariance flux measurements (EC). EC is the most direct micrometeorological method for measuring vertical fluxes in the turbulent mixed planetary boundary layer (PBL), and relies on the measurement of the covariance of chemical concentration with vertical wind speed [92]. However, EC method requires that VOC measurements are as fast or faster than the vertical wind is changing direction, a requirement that is conceivable when using PTR-MS [29]. The main drawback of this technique is that it cannot distinguish between isobaric species, which is a major downside concerning atmospheric measurements since these species are commonly present in the atmosphere in significant quantities (e.g.

monoterpenes) [93]. GC-MS allows to resolve the superimposing signals generated by isobaric ions in PTR-MS, conferring a highly specific compound identification [94]. However, GC-MS also has a lower time resolution when compared to PTR-MS [94]. For that reason, both instruments have been used in a complementary manner for atmospheric characterization of VOCs in the atmosphere [88, 95].

3 Experimental methods

This section describes the chemicals (Table 1), instruments and other equipment (Table 2), methods and experimental conditions used in this thesis. More detailed information is available in Papers I-IV.

Table 1. *List of chemicals used in this thesis.*

Compound	Supplier	Purity	Paper
Calion™ PV standard Mix	Torion Technologies Inc. (American Fork, Utah, USA)		I, II, III
Helium	AGA (Espoo, Finland)	99.996%	I, II, III, IV
CO_2	AGA (Espoo, Finland)	SFE-grade	II
Nitrogen	AGA (Espoo, Finland)	99.9%	II
α-Pinene	Sigma-Aldrich (St. Louis, MO, USA)	98%	I, II, III, IV
(−)-β-Pinene	Sigma-Aldrich (St. Louis, MO, USA)	≥99%	III
(+)-Camphene	Sigma-Aldrich (St. Louis, MO, USA)	≥90%	III
(+)-3-Carene	Fluka (Steinheim, Germany)	>98.5%	I
(+)-3-Carene	Sigma-Aldrich (St. Louis, MO, USA)	>98.5%	II, III, IV
R-(β)-Limonene	Fluka (Steinheim, Germany)	≥99%	I
Pinonaldehyde	Synthesized according to [96]		II
Pinanediol	Sigma-Aldrich (St. Louis, MO, USA)	99%	II
Hexanal	Accustandard (New Heaven, CT, USA)	98%	II
Heptanal	Accustandard (New Heaven, CT, USA)	98.5%	II
Octanal	Accustandard (New Heaven, CT, USA)	100%	II
Octanal	Sigma-Aldrich (St. Louis, MO, USA)	99%	III, IV
Nonanal	Accustandard (New Heaven, CT, USA)	96%	II
Nonanal	Sigma-Aldrich (St. Louis, MO, USA)	≥95%	III, IV
Decanal	Accustandard (New Heaven, CT, USA)	96%	II
Decanal	Sigma-Aldrich (St. Louis, MO, USA)	≥98%	III, IV
Benzaldehyde	Accustandard (New Heaven, CT, USA)	98.5%	II
Ethylbenzene	Sigma-Aldrich (Milwaukee, WI, USA)	99%	II
p-Xylene	Sigma-Aldrich (Milwaukee, WI, USA)	≥99%	II
m-Xylene	Merck (Darmstadt, Germany)	≥99.3%	II
Isopropanol	Fisher Scientific (Loughborough, UK)	99.96%	III
Dichloromethane	Fisher Scientific (Loughborough, UK)	99.99%	IV
Ultrapure water	(purified with DirectQ-UV)		I, II, III
Dimethylamine hydrochloride	Sigma-Aldrich (St. Louis, MO, USA)	99%	I, II

Table 1. *List of chemicals used in this thesis (Continued).*

Compound	Supplier	Purity	Paper
Ethylamine hydrochloride	Sigma-Aldrich (St. Louis, MO, USA)	98%	I
Potassium hydroxide (5 M)	J.T. Baker (Gothenburg, Sweden)		I
Sodium hydroxide (0.1 M)	FF-Chemicals Ab (Yli li, Finland)		II

Table 2. *List of instruments and equipment used in this thesis.*

Instruments/Equipment	Manufacturer	Paper
Agilent 5973 N mass selective detector	Agilent Technologies (Palo Alto, CA, USA)	III, IV
Agilent 5975 C mass selective detector	Agilent Technologies (Palo Alto, CA, USA)	II, IV
Agilent 6890 N gas chromatograph	Agilent Technologies (Palo Alto, CA, USA)	II, III, IV
Air sampling pump	BUCK Elite (Orlando, FL, USA)	II
Box-type Soil chambers (80 cm×40 cm×25 cm)	-	III
Fan	Sunon (Beijing, China)	I, III
CUSTODION® SPME syringes (PDMS/DVB, 65 μm)	Torion Technologies Inc. (American Fork, Utah, USA)	I, II, III
CUSTODION® SPME syringes (PA, 85 μm)	Torion Technologies Inc. (American Fork, Utah, USA)	III
CUSTODION® SPME syringes (CAR/PDMS, 85 μm)	Torion Technologies Inc. (American Fork, Utah, USA)	III
CUSTODION® SPME syringes (DVB/CAR/PDMS, 50/30 μm)	Torion Technologies Inc. (American Fork, Utah, USA)	III
CUSTODION® NTME syringes (Tenax TA (1 mg, 60–80 mesh), Carboxen 1016 (1.6 mg , 60– 80 mesh), and Carboxen 1003 (1.5 mg, 60–80 mesh))	Torion Technologies Inc. (American Fork, Utah, USA)	II
Deactivated fused silica retention gap (1.5 m × 0.53 mm (i.d.))	Agilent Technologies (Palo Alto, CA, USA)	II, III, IV

Table 2. *List of instruments and equipment used in this thesis (Continued).*

Instruments/Equipment	Manufacturer	Paper
Dynamic air sampling system for SPME	Laboratory-made	I, III
Dynamic air sampling system for SPME Arrow	Laboratory-made	IV
Headspace vials (20 mL)	Phenomenex (Torrance, CA, USA)	I, II, III, IV
HP-5MS GC column (30 m × 0.25 mm x 0.25 µm)	Agilent Technologies (Palo Alto, CA, USA)	IV
Inert-Cap for Amines (30 m × 0.25 mm (i.d.))	GL Sciences (Tokyo, Japan)	II, III,
Low thermal mass capillary column (MXT-5, 5 m, 0.1 mm, 0.4 µm d_f)	Torion Technologies Inc. (American Fork, Utah, USA)	I, II, III
19-gauge Merlin Microseal	Merlin Instrument Company (Half Moon Bay, CA, USA)	II
23-gauge Merlin Microseal	Merlin Instrument Company (Half Moon Bay, CA, USA)	I, II, III, IV
Merlin nut	Merlin Instrument Company (Half Moon Bay, ,CA, USA)	I, II, III, IV
Millipore water purifier	Millipore S.A. (Billerica, MA, USA)	I, II, III
Monotherm heatable magnetic stirrer	Variomag Electronicrührer, Labortechnik (Munich, Germany)	II, III
NTME air sampling interface	Torion Technologies Inc. (American Fork, Utah, USA)	II
0.45 µm Nylon filter	Nalgene (Rochester, NY, USA)	II
Permeation oven	Laboratory-made	IV
Portable GC-MS (TRIDION™-9)	Torion Technologies Inc. (American Fork, Utah, USA)	I, II, III
Press-fit connector	BGB Analytik (Böckten, Switzerland)	II, III, IV
PTR-QMS	Ionicon Analytik (Innsbruck, Austria)	I, III
Sampling case	Pas Technology (Magdala, Germany)	II

Table 2. *List of instruments and equipment used in this thesis (Continued).*

Instruments/Equipment	Manufacturer	Paper
SARTORIUS BP301S Analytical balance	SARTORIUS (Gottingen, Germany)	II, III, IV
SPME fibers (PDMS/DVB, 65 μm)	Supelco (Bellefonte, PA, USA)	IV
SPME fibers (PDMS/Carbon WR, 95 μm)	CTC Analytics AG (Zwingen, Switzerland)	IV
SPME Arrow (PDMS/Carbon WR, 120 μm)	CTC Analytics AG (Zwingen, Switzerland)	IV
SPME Arrow (PDMS/DVB, 120 μm)	CTC Analytics AG (Zwingen, Switzerland)	IV
Standard inlet septum, 11 mm	BGB Analytik (Zurich, Switzerland)	IV
Standard inlet septum, 11 mm	Agilent Technologies (Palo Alto, CA, USA)	IV
10 L Tedlar® Teflon bag	Sigma Aldrich (St. Louis, MO, USA)	II
UltraClean 18 mm screw cap with septa	Phenomenex (Torrance, CA, USA)	I, II, III, IV
ZB-5MS GC column (30 m × 0.25 mm × 0.25 μm)	Phenomenex (Torrance, CA, USA)	III

3.1 Sampling site

The studies reported in this work were performed at the SMEAR II boreal forest measurement station (Station For Measuring Ecosystem-Atmosphere Relations, 61°50.845′ N, 24°17.686′ E, 179 m above sea level) in Hyytiälä, located in southern Finland [97]. The station is situated in an approximately 55 years old Scots pine stand, of about 21 m canopy height and 1170 ha^{-1} of average tree density [98]. The forest soil is Haplic podzol, formed in a glacial till, with an average depth of 0.5-0.7 m above the bedrock [99].

Tampere, a city with around a half of million inhabitants, is located 60 km south-west from the SMEAR II station. Major sources of air pollutants from urban areas in Finland include wood combustion and traffic, and long-range atmospheric transport can occasionally contribute to their atmospheric levels at SMEAR II station [100-102]. Different tree species (mainly pines and spruces) in the surrounding forest and two sawmills located 6.3 km south-east from the sampling site can equally influence the local atmospheric composition [50, 103, 104]. These sawmills produce together more than 400 000 m^3 per year of sawn timber.

3.2 Sample collection

SPME-based sampling techniques were used for the analysis of VOCs at the boreal forest sampling site. The collection of VOCs in the atmosphere was performed by using dynamic SPME (Paper I) and NTME (Paper II). SPME was additionally used for the characterization of BVOC species measured in soil chambers (Paper III). A novel SPME Arrow sampling system was also tested for the collection of VOCs in the boreal forest air (Paper IV).

In Paper I, SPME sampling was performed from the 15th to 19th of June in 2013, corresponding to the period of the year when BVOC emissions are expected to be high due to the high temperatures and solar radiation. A total of four air samples were collected daily from 8 am to 4 pm, to cover the period of time with most frequent occurrence of nucleation events. Each sample was collected during 2 hours to maximize the enrichment of VOCs on the sorbent material. Analytes were collected on a PDMS/DVB coated SPME fiber, which has been successfully employed for the collection of VOCs in other studies preceding this research [105]. In our study, a self-made dynamic air sampling system was used, which consisted of a small cooling fan for dragging air around the SPME fiber inserted inside a laboratory-made polyacetal plastic block (Fig. 11). As compared to static collection mode, this sampling system accelerated the kinetics of extraction, increasing the amounts of atmospheric analytes collected on the SPME fiber prior to equilibrium.

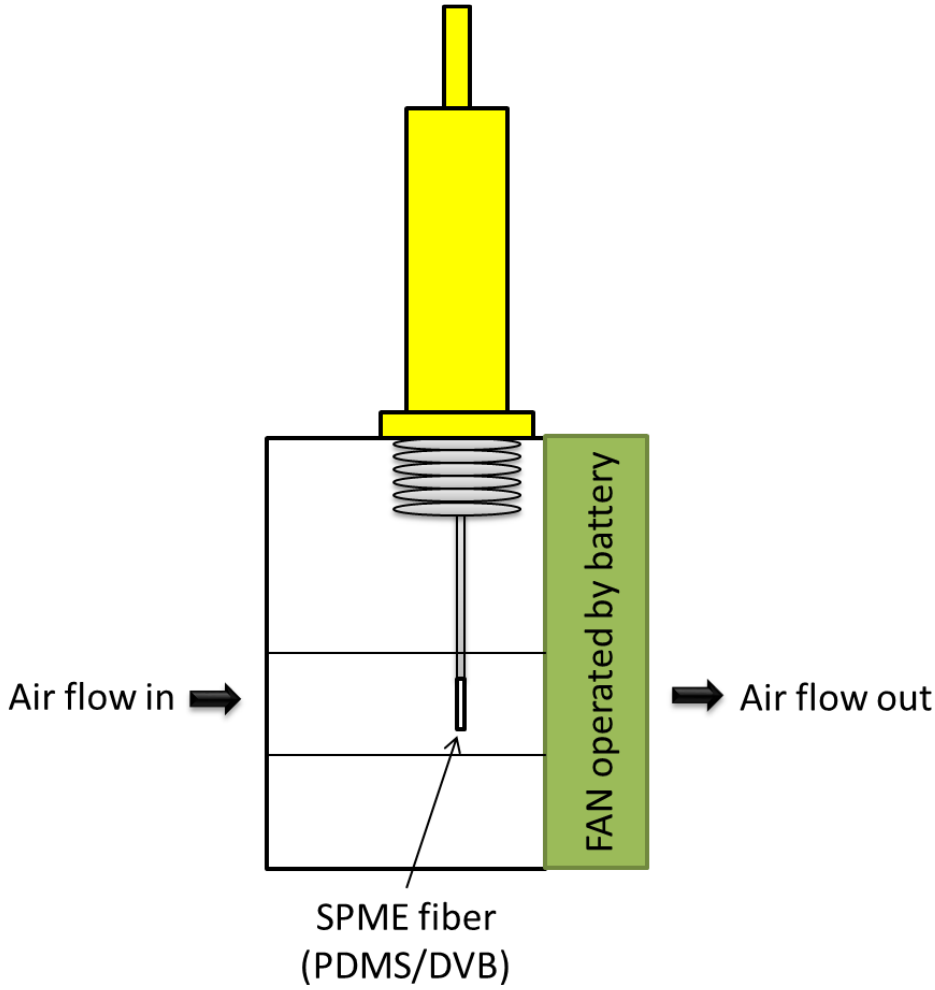

Figure 11. *Dynamic air sampling system for SPME (Paper I).*

NTME was also used for the sampling of VOCs at the SMEAR II station ecosystem (Paper II). Samples were collected in mid-summer and autumn 2014. The first part of the sampling campaign, occurred from the 12th June to 10th July, was intended to test the potential of NTME for qualitative and semi-quantitative measurement of VOCs. The purpose of the second part of the campaign, which took part from the 3rd to 12th of November, was to apply the method previously developed to study the effect of the snow pack on the concentration of VOCs in the air. Sampling was performed with needle trap microextraction devices, packed with Tenax TA, Carboxen 1016 and Carboxen 1003. These devices contained a side-hole for dynamic sampling and were installed in a commercial air sampling interface for NTD (Fig. 12). The air was pre-filtrated through a 0.45 µm nylon filter to prevent the blocking of the needle by aerosol particles and other impurities. Analytes

were dynamically extracted onto the NTD by using a sampling flow rate of 25 mL min^{-1}. The collection volume selected was 2.5 L.

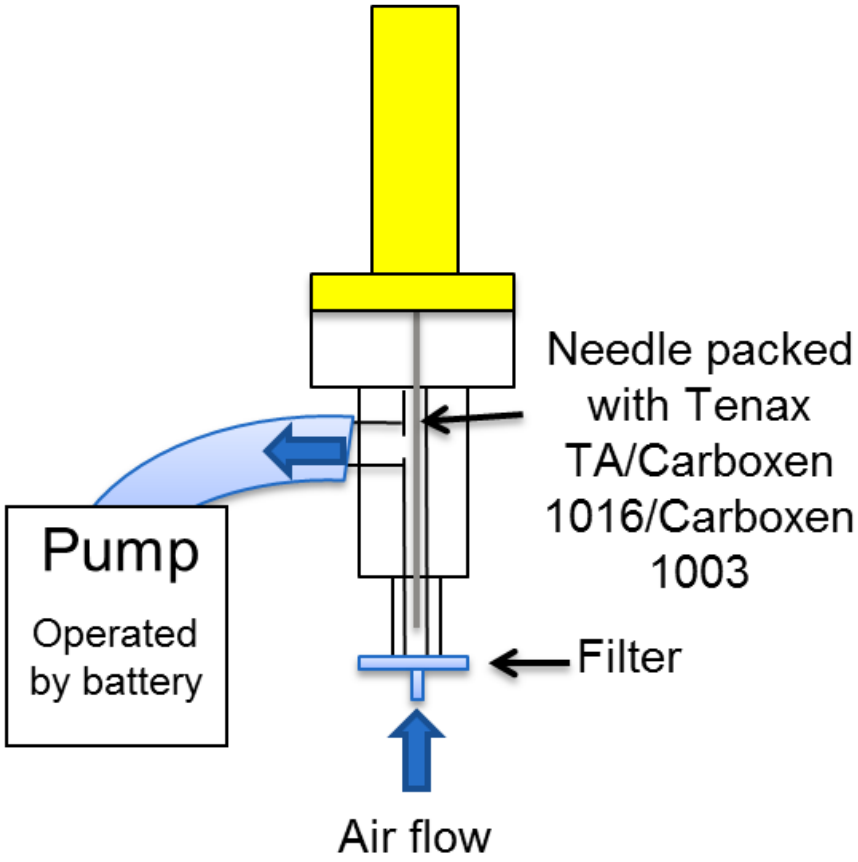

Figure 12. *Schematic representation of the collection system used for needle trap microextraction device (Paper II).*

In the same study, the breakthrough volume of the NTD was of concern due to the trace levels of studied compounds in ambient air and the consequent need of high sampling volumes. Thus, breakthrough values given by manufacturers were considered when choosing the sampling volume. Two laboratory studies were also performed, where 1 µL of α-pinene was inserted in a 20 ml headspace vial, evaporated by applying heat and 0.5 ml were subsequently transferred to a 10 L Teflon bag filled with nitrogen. In the first study, 2, 2.5 and 3 L were collected sequentially, which corresponded to the extraction volumes used during the field campaign. The second study, consisting in the collection of eight different volumes ranging from 0.5 to 9 L, was performed to test the extraction capability of the NTD packing materials. The final concentration was 386 ppbV, which is significantly higher than the concentrations commonly measured in ambient air.

SPME was also used for the characterization of BVOCs in chambers installed at the forest soil and in ambient air (Paper III). Samples were collected and analysed in summer 2015. The sampling campaign was divided into two parts. In the first part of the campaign, which occurred from the 23th to 28th of June, the method was optimized and tested. The optimization covered the evaluation of different SPME materials, fiber-to-fiber variability studies, the sampling time inside the chambers and the ambient air collection time. Samples were analysed by portable GC-MS. A comparison between portable and conventional GC-MS analysis was also performed by sampling passively with two syringes from the same chambers, followed by further analysis with both systems. During the second part of the campaign, from the 5th to 27th of August, samples were collected by the optimized method. Sampling was performed by using SPME fibers coated with PDMS/DVB.

The soil chambers, placed 10 to 30 m apart from each other, were installed atop of collars located at the forest floor. The forest floor flora inside the soil chambers (Fig. 13) was composed of a mixture of herbaceous species, mostly small-sized grasses and dwarf shrubs, such as lingonberry (*Vaccinium vitis-idaea L.*) and bilberry (*Vaccinium myrtillus L.).* The soil was also fully covered by a mixture of moss species. The dominant forest floor vascular plant species in chambers 13 and 15 were lingonberry and bilberry, whereas in chamber 10 the dominant vascular plant was twinflower (*Linnaea borealis L.).* The forest cover over the chambers was rather homogeneous with almost closed canopy layer, but vascular plant coverage in chamber 10 was lower compared to the other two chambers used in this study.

Figure 13. *Soil chambers (10, 13 and 15 respectively) used during the sampling campaign (Paper III).*

The SPME-GC-MS method was optimized by studying first the extraction efficiency of different SPME fiber materials for the selection of the most suitable sorbent for BVOC collection. Four different materials were tested, which consisted of PDMS/DVB, PDMS/DVB/CAR, PDMS/CAR and PA. Standard solutions (500 μg/mL) of α-pinene and

Δ^3-carene in an isopropanol/water mixture were used. Isopropanol was used for the preparation of stock solutions that were further diluted to the final trace concentration with water. Headspace sampling was performed after vials were equilibrated for 30 minutes under vigorous agitation. Extraction time from soil chambers was optimized to improve pre-concentration of the studied compounds. The extraction times studied were 30 and 45 minutes and the experiment was performed twice. Sampling time of the dynamic SPME was also optimized by inserting three different fibers in dynamic sampling systems for SPME, measuring the flow rates of the different systems and collecting ambient samples for 20, 40 and 60 minutes. The experiment was carried out two times.

The final sampling method included the following steps: closing the chambers for 5 minutes, insertion of SPME fibers inside the chambers and subsequent static collection during 40 minutes (Fig. 14). The air flow through the chambers was stopped during the sampling procedure to allow the increase of analyte concentrations throughout the sampling period, assuming that emissions are higher than sinks. With this approach, concentrations were expected to differ to a great extent from the ambient concentrations after the 5 minutes of closure. Ambient samples were collected during 60 minutes by two laboratory-made dynamic sampling systems for SPME, installed about 30 cm above the ground vegetation. Dynamic collection was preferred for ambient sampling, since VOC mass loading on the fiber increases with an increase in wind velocity from 0 to 5 cm/s [56].

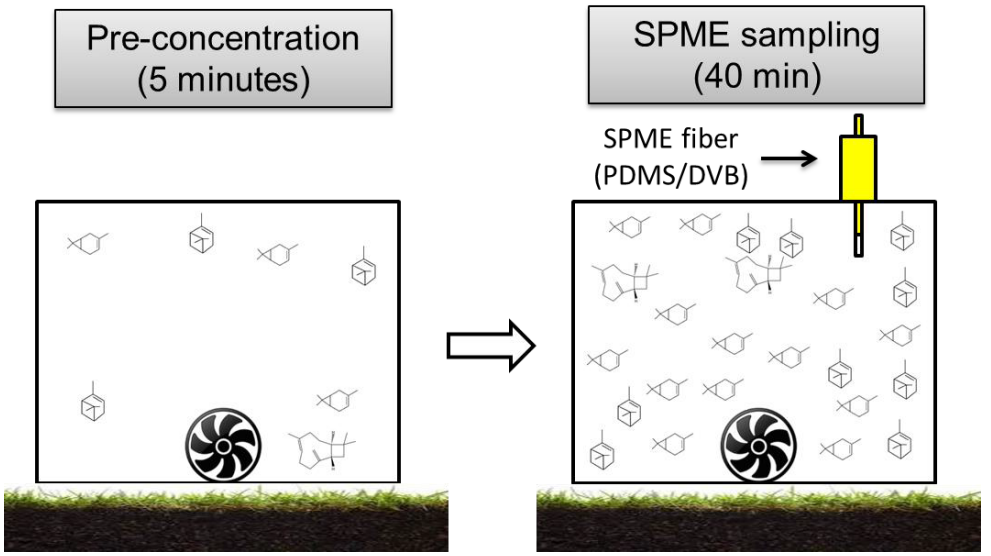

Figure 14. *SPME collection of BVOCs from soil chambers.*

In Paper IV, a novel SPME Arrow was used for the collection of BVOCs in ambient air and field measurements were complemented with laboratory tests. The aim of this study was to investigate the advantages of this technique when compared to those of conventional SPME fibers.

The purpose of laboratory tests was to study the extraction profiles obtained with the referred SPME-based techniques, to compare their extraction efficiencies, and to evaluate the effect of meteorological parameters (temperature and relative humidity) on the extracted amounts of target BVOCs. A laboratory-made diffusion oven was used to generate known and constant concentrations of gaseous standards. Diffusion vials were also prepared in the laboratory by adding a small amount of studied compounds (α-pinene, Δ^3-carene, octanal and decanal) to headspace vials and piercing a small portion of a deactivated fused silica capillary through the cap to allow constant diffusion from the vials.

Air samples were collected and analysed on-site, from the 11th to 15th of August, 2017. Three SPME systems, including two SPME Arrows (PDMS/Carbon WR and PDMS/DVB) and one SPME fiber (PDMS/DVB), were used for static collection from the ambient air. Additionally, an SPME Arrow coated with PDMS/DVB was simultaneously used for dynamic collection with a laboratory-made dynamic sampling system (Fig. 15). This device was modified from the sampling system developed in Paper I. Analytes were then collected during 45 minutes. The GC-MS response was calibrated with authentic standards.

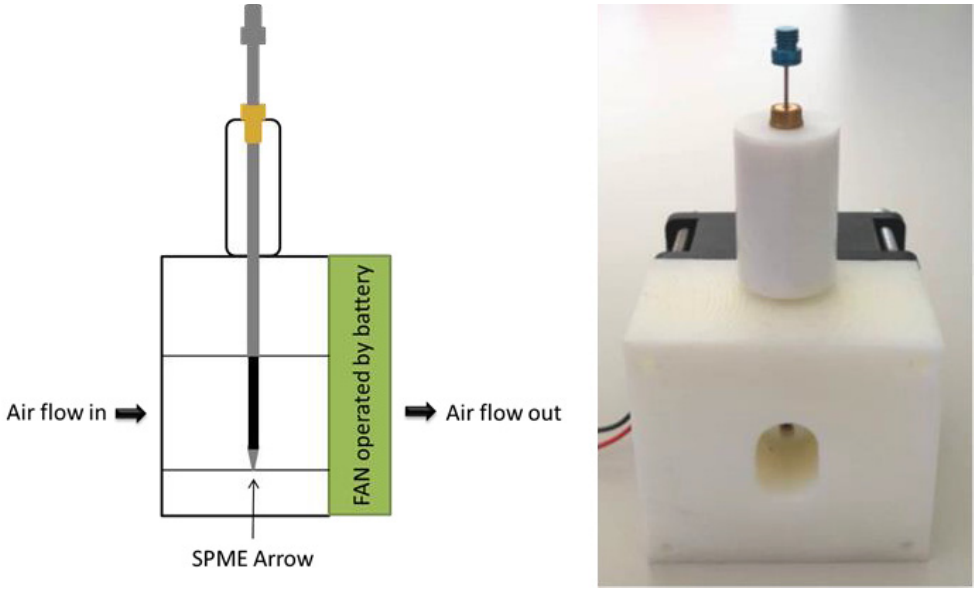

Figure 15. *Dynamic sampling system developed for the collection of BVOCs from ambient air with SPME Arrow (Paper IV).*

3.3 Measurement of volatile organic compounds

3.3.1. Gas chromatography-mass spectrometry measurements

Conventional and portable GC-MS were applied during this study for the measurement of VOCs. The analytical conditions used in the laboratory and field measurements are summarized in Tables 3 and 4 respectively, including the type of column, separation conditions and analytical instrument. More information is present in the referred Papers.

Table 3. *Analytical conditions used during laboratory measurement of VOCs.*

Paper	Column type	Analytical conditions	Instrument
II	MXT-5 (5 m x 0.1 mm x 0.4 µm)	desorption: 10 s, 270 °C; split ratio: 10:1 (at 2 s)- 50:1 (from 10-30 s); T.P.: 50 °C (10 s) – 2 °C/s -270 °C (50 s); mass range: 43-500 amu (EIC).	portable GC-MS
II	Inert-Cap for Amines (30 m × 0.25 mm)	desorption: 3 min, 250 °C; split ratio: splitless (2 min, lower volumes), 10:1 (higher volumes); T.P.: 40 °C (1 min) – 20 °C/min -250 °C (4.5 min); mass range: 30-400 amu (EIC).	GC-MS (Agilent 5975 C)
III	ZB-5MS (30 m x 0.25 mm x 0.25 µm)	desorption: 10 s, 250 °C; split ratio: splitless (2 min); T.P.: 50 °C (2 min) – 20 °C/min -250 °C (4 min); mass range: 27-100 amu (EIC).	GC-MS (Agilent 5973 N)
IV	HP-5MS (30 m x 0.25 mm x 0.25 µm)	desorption: 5 min, 270 °C; split ratio: splitless (2 min); T.P.: 50 °C (1 min) – 20 °C/min -250 °C (1 min); mass range: 30-400 amu (EIC).	GC-MS (Agilent 5973 N, Agilent 5975 N)

Table 4. *Analytical conditions used during field measurement of VOCs.*

Paper	Column type	Analytical conditions	Instrument
I	MXT-5 (5 m x 0.1 mm x 0.4 µm)	desorption: 10 s, 270 °C; split ratio: 10:1 (at 5 s)- 50:1 (at 30 s); T.P.: 50 °C (10 s) – 2 °C/s -270 °C (50 s); mass range: 43-500 amu (EIC).	portable GC-MS
II	MXT-5 (5 m x 0.1 mm x 0.4 µm)	desorption: 10 s, 270 °C; split ratio: 10:1 (at 2 s)- 50:1 (from 10-30 s); T.P.: 50 °C (10 s) – 2 °C/s -270 °C (50 s); mass range: 43-500 amu (EIC).	portable GC-MS
III	MXT-5 (5 m x 0.1 mm x 0.4 µm)	desorption: 10 s, 270 °C; split ratio: 10:1 (at 5 s)- 50:1 (from 10-30 s); T.P.: 50 °C (10 s) – 2 °C/s -270 °C (50 s); mass range: 43-500 amu (TIC).	portable GC-MS
III	Inert-Cap for Amines (30 m × 0.25 mm)	desorption: 10 s, 250 °C; split ratio: splitless (2 min); T.P.: 50 °C (2 min) – 20 °C/min -250 °C (4 min); mass range: 40-300 amu (TIC).	GC-MS (Agilent 5973 N)
IV	HP-5MS (30 m x 0.25 mm x 0.25 µm)	desorption: 5 min, 270 °C; split ratio: splitless (2 min); T.P.: 70 °C (1 min) – 20 °C/min -250 °C (1 min); mass range: 30-400 amu (EIC).	GC-MS (Agilent 5973 N)

3.3.2. Proton-transfer-reaction-quadrupole mass spectrometry measurements

Continuous measurements by proton-transfer-reaction-quadrupole mass spectrometer (PTR-QMS) were also performed in this study for comparison purposes (Paper I and III). The on-line VOC flux measurements were conducted following the scheme described elsewhere [99]. The automatic, dynamic gas-exchange measurement system consisted of sampling tubing, analyzers and different types of enclosures, including the three box-type soil chambers (volume 80 dm^3) used in this study. The enclosure remained mostly open, being only closed intermittently for 450 seconds every third hour and during the measurements performed in this study. When the enclosures were open, their interior was in contact with unfiltered ambient air. During closure episodes, sample air was drawn from the enclosure into the gas analyzers along the sample tubes.

Air temperature inside the enclosure was measured before and during the closure, recording the values at 5s intervals. The VOC sub-sample (0.1 dm^3 min^{-1}) for PTR-QMS was taken from a sample tube with a flow rate of 1.1 dm^3 min^{-1}. A heated FEP-tubing of 64 m length (i.d. 4 mm) was used as a high flow sample tube. The sub-sample for a high sensitivity PTR-QMS was drawn from the high flow sample tube through a polytetrafluoroethylene (PTFE) tube (i.d. 1.57 mm and length of about 5 meters).

PTR-QMS measures the total concentration of all compounds that have equal atomic mass with a resolution of 1 amu (atomic mass unit) and adequate proton affinity. Background signals were corrected by subtracting the measured instrumental background (air purified using a Parker ChromGas Zero Air Generator, model 3501, Parker Hannifin, Ohio, Cleveland, USA) from the measured volume mixing ratios. The calibration of PTR-QMS was conducted two to three times per month to correct the changes in sensitivity over the mass range. The standard gases contained 1 ppmv of methanol, acetaldehyde, acetone, isoprene, α-pinene and several other compounds (Apel-Riemer Environmental Inc., USA). A zero air generator was used for diluting the standard gas close to the atmospheric concentrations, of 5 ppbv.

The monoterpene measurement was based on the ratio of m/z 137. Volume mixing calculation method and the basis for calibration are described elsewhere [106]. Flux rate calculation method and evaluation of chamber method for VOC measurements are described in another study [107]. Soil chamber measurement method [99] and a description of the current practical operation of the measurement system are given elsewhere [27]. The risk of overlapping due to the generation of sesquiterpene fragments of the same m/z as used for monoterpenes quantitation was neglected, since there is an order of magnitude difference in the relative emission profiles of monoterpene and sesquiterpenes sources [102] and the reactivity of sesquiterpenes will cause their losses in the long sampling lines used.

4 Results and discussion

The objective of this work was to use new solid-phase microextraction based sampling techniques combined with gas chromatography-mass spectrometry for the rapid analysis of VOCs in the atmosphere (Papers I, II, and IV). The method developed in Paper I was further applied to solve research questions related with BVOC emissions (Paper III), which will be described further ahead. This section summarizes the main findings obtained from the laboratorial studies and boreal forest measurements. More detailed information is present in the original articles.

4.1 Measurement of biogenic volatile compounds in the atmosphere: dynamic solid-phase microextraction and portable gas chromatography-mass spectrometry

The gas-phase oxidation of BVOCs produces a large diversity of oxidation products, and the type of products formed and their yields will depend on the structure of BVOCs and consequent reactivity with atmospheric oxidants [31]. Furthermore, the specific compounds resulting from photooxidative reactions will have a different effect on the atmospheric nucleation efficiency [108]. For these reasons, BVOCs speciation is a key to understand their impact on atmospheric chemistry. This is particularly important for monoterpenes due to the assortment of species that can be produced and emitted by terrestrial vegetation and their global annual flux of about 11%, constituting as a whole the second most emitted BVOCs to the atmosphere following isoprene [2].

The field analysis of monoterpene species usually consists in the sampling of these species onto adsorbent tubes filled with a combination of sorbent materials (generally Tenax TA/Carbopack-B), followed by their thermodesorption into a gas chromatograph-mass spectrometer [5]. In order to develop an analytical system that is completely portable and that allows the measurement of BVOCs in practically all environmental conditions without the demand for various resources/infrastructures is often lacking at many remote sites, the applicability of dynamic SPME combined with portable GC-MS was evaluated in this study (Paper I).

As demonstrated in Fig. 16, the analysis revealed the presence of the most abundant monoterpene species at the sampling site, including α-pinene, Δ^3-carene and limonene. Results were in good agreement with the total monoterpene concentration simultaneously measured by PTR-MS, which was exploited for the validation of the analytical method employed in this study. The concentrations of separated monoterpenes were calculated by determining each monoterpene as percentage from the sum of all monoterpene peak areas obtained by GC-MS and multiplying each fraction by the total concentration obtained by PTR-MS (Fig. 17).

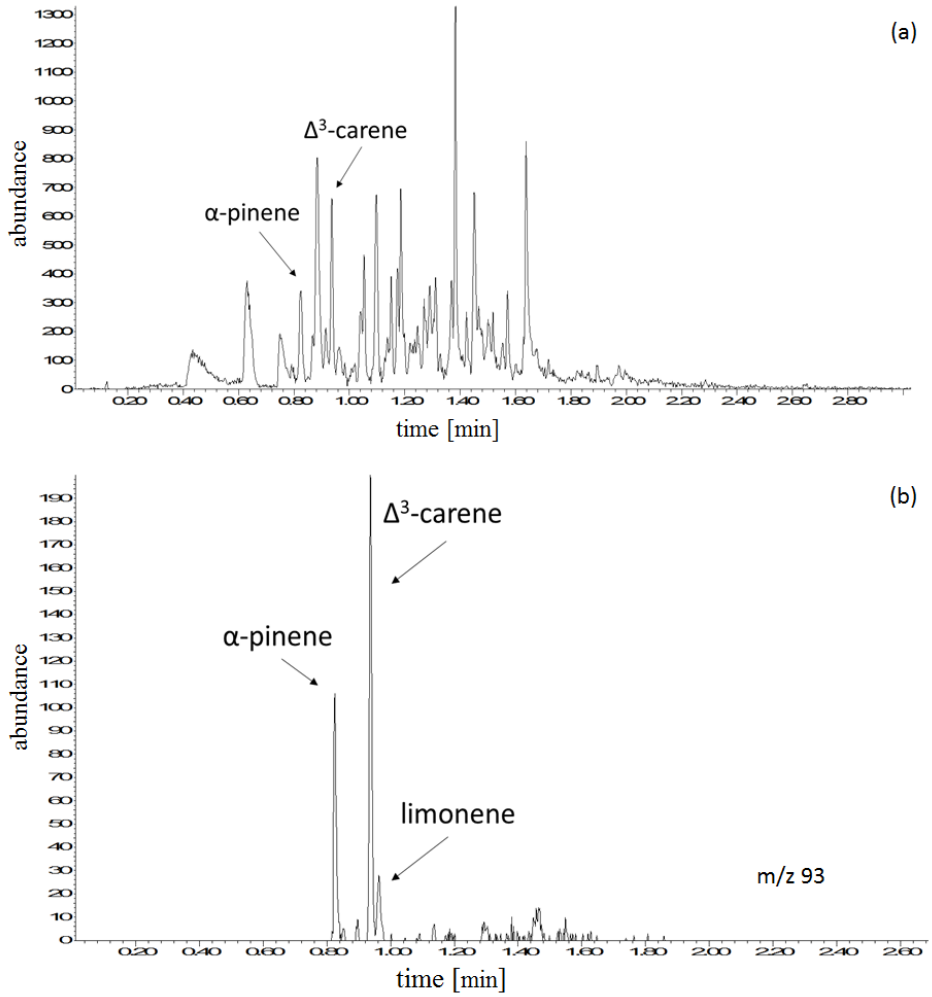

Figure 16. *Total ion chromatogram (TIC) (a) and extracted ion chromatogram (EIC) (b) obtained for a sample collected and analysed by SPME-GC-MS during the sampling campaign.*

The effect of temperature and relative humidity on the results achieved was also evaluated. Higher amounts of monoterpenes were observed when ambient temperature was high. This result is consistent with the known temperature-dependence of monoterpene emission rates from the boreal forest vegetation [109]. Interestingly, monoterpene amounts were lower at high relative humidity. This effect coincided with a low temperature, which can explain per se the finding due to the fact that monoterpene emissions are mostly driven by temperature during summer. However, the existence of a sink effect caused by humidity cannot be excluded, since these compounds are soluble in water at low concentrations. Complementary studies performed under controlled laboratory conditions are still required to confirm this hypothesis.

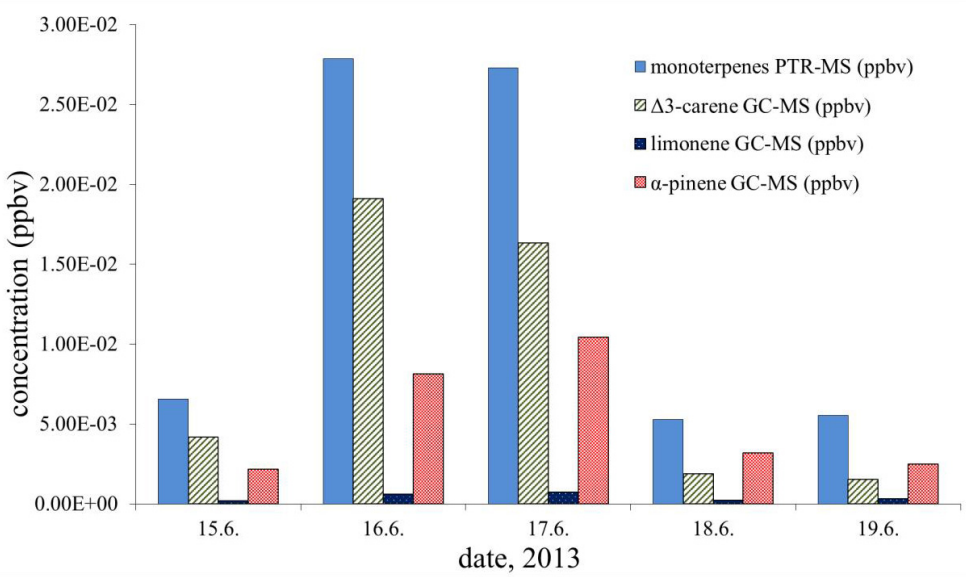

Figure 17. *Median daily concentrations of monoterpenes analysed by GC-MS (scaled from PTR-MS) and median daily total concentration of monoterpenes determined by PTR-MS (ppbv) (Paper I).*

The relatively high vapor pressure of some of the monoterpene oxidation products, such as pinonaldehyde and pinonic acid, allows them to be present in the gas-phase [19]. In this study, these α-pinene oxidation products were also tentatively identified and measured. The averaged peak area values obtained during different times of the day revealed that the amount of α-pinene increased during the periods of time when temperatures and solar radiation were higher while amounts of its oxidation products decreased (Fig. 18). This result is consistent with the contribution of these compounds to SOA formation.

The simultaneous analysis of different monoterpene species and their primary oxidation products is important to associate the corresponding products with the precursor compounds. Further improvements in the developed method, particularly concerning the quantitation of measured compounds and the assessment of on-fiber oxidation, could allow to correlate the mixing ratios of specific monoterpenes with those obtained for their oxidation products. This correlation would result in real-time information about monoterpene atmospheric reactivity, since it depends on the structural features of each monoterpene precursor, and then complement the knowledge obtained with PTR-MS that cannot separate the measured monoterpene species.

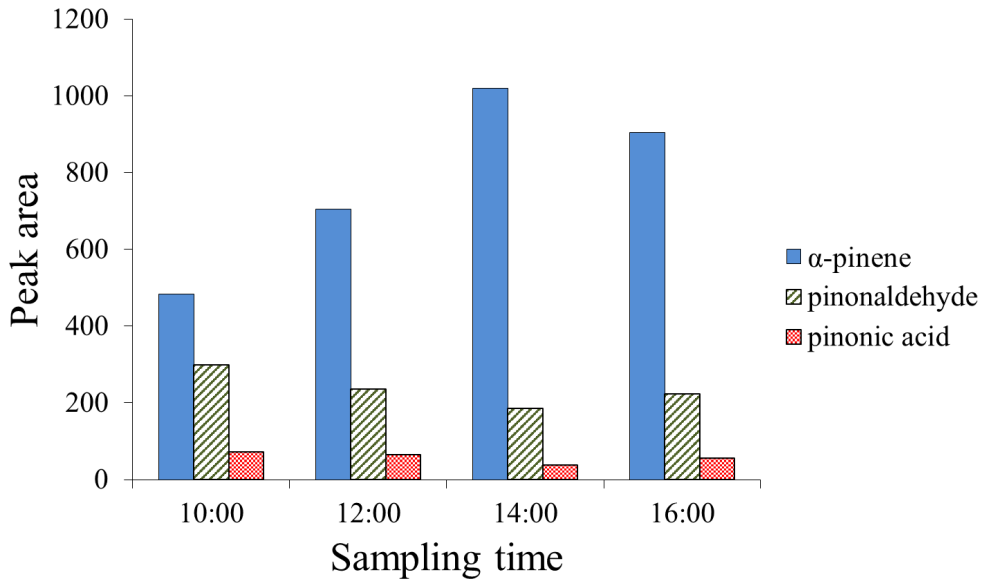

Figure 18. *Daily variation of the amounts (peak area values) of pinonaldehyde, pinonic acid and α-pinene measured by SPME-GC-MS (Paper I).*

4.2 Potential of needle trap microextraction-portable gas chromatography-mass spectrometry for the measurement of atmospheric organic volatiles

VOCs can also be sampled by using a NTME system. This technique has the joint advantages of solid-phase extraction (SPE) and SPME, such as the sensitivity that can be improved by increasing the sampling volume and being an exhaustive technique like SPE without sacrifying the advantages of small sample sizes offered by SPME [110]. The NTME systems are also considered more robust than SPME, since the sorbent particles are protected inside a steel needle [111].

For all the pointed reasons, the potential of NTME combined with portable gas chromatography-mass spectrometry for fast on-site measurement of VOCs was evaluated in Paper II. A semi-quantitative approach was used due to difficulties in the preparation of gaseous standard solutions at accurate concentration for calibration purposes. Target compounds included monoterpenes, aldehydes, BTEX and amines because of their contribution to atmospheric photochemistry. For the selected analytes, identification was confirmed with authentic standards (Table 5).

Table 5. *Retention times and most abundant fragments (in order of descending intensity) obtained by portable GC-MS for the identified compounds (Paper II).*

Compound	R.T. (min)	Fragmentation pattern with portable GC-MS	Fragmentation pattern obtained from NIST library
Monoterpenes			
α-pinene	0.82	93 (100), 92, 91, 53, 79	93 (100), 91, 92, 39, 77
Δ^3-carene	0.93	93 (100), 91, 79, 92, 80	93 (100), 91, 92, 39, 77
Aldehydes			
benzaldehyde	0.87	105 (100), 53, 107, 106, 77	77 (100), 106, 105, 51, 50
hexanal	0.60	56 (100), 57, 67, 83,72	44 (100), 56, 41, 43, 57
heptanal	0.76	55 (100), 71, 97, 70, 44	70 (100), 41, 44, 43, 55
octanal	0.91	69 (100), 111, 57, 67, 56	43 (100), 44, 41, 56, 84
nonanal	1.05	57 (100), 143, 67, 69, 81	57 (100), 41, 43, 56, 44
decanal	1.19	81 (100), 67, 83, 69, 57	43 (100), 41, 57, 55, 44
pinonaldehyde	1.30	151 (100), 83, 107, 97, 109	83 (100), 69, 43, 98, 55
BTEX			
ethylbenzene	0.70	91 (100), 106, 92, 78, 65	91 (100), 106, 51, 65, 77
p-xylene	0.72	91 (100), 106, 105, 79, 119	91 (100), 106, 105, 77, 51
m-xylene	0.72	91 (100), 106, 105, 107,65	91 (100), 106, 105, 77, 51
Amines			
dimethylamine	0.17*	44 (100), 46, 45, 43, 42	44 (100), 45, 28, 42, 43

** no retention in the column (t_M=0.12 min).*

A slight difference in the fragmentation was found between the conventional and portable GC–MS, especially for the compounds that were more extensively fragmented. This finding can be explained by the different types of mass analysers used in the conventional and portable GC–MS, being in this study a quadrupole and a toroidal ion trap respectively. The obtained result clearly demonstrated that the clarification of fragmentation patterns, with recourse to standards, is necessary when using portable GC-MS instrumentation for the correct identification of analytes in the samples and for a reliable semi-quantitative/quantitative data analysis. This is particularly important when using auxiliary spectral library search, such as NIST 2014.

Several compounds were tentatively identified upon analysis of samples, including the most abundant monoterpenes (α-pinene and Δ^3-carene) at the studied boreal forest site, aldehydes and anthropogenic compounds belonging to the BTEX group. Contrary to the results obtained in the Paper I, where PDMS/DVB coated SPME fibers were used, α-pinene was the most abundant compound in this study. This result demonstrated some adsorption selectivity towards Δ^3-carene when performing the referred equilibrium-based SPME fiber measurements. Monoterpene amounts were consistent with the increase in temperature, which has also been observed in Paper I and explained by the temperature-dependence of monoterpene emissions previously described at the same sampling site [109].

The aldehydes identified in this study were hexanal, heptanal, octanal, nonanal, decanal and benzaldehyde. Oppositely to what was observed for monoterpenes, temperature could

not explain the changes in atmospheric amounts of these compounds. However, a good correlation was found between all the measured aldehydes, which suggested that they are emitted from the same sources as a response to similar biological/atmospheric processes. An exception was discovered for pinonaldehyde due to its distinct formation processes linked to the atmospheric oxidation of α-pinene.

The influence of measured BVOCs on atmospheric particle number concentration (PNC) was also evaluated. As seen from Fig. 19, the amounts of α-pinene and pinonaldehyde were lower during days when PNC was higher, supporting the role of α-pinene oxidation products in new particle formation. The amounts of aldehydes were also lower during days when PNC increased, suggesting that these compounds can have an influence on nucleation.

Anthropogenic VOCs, in particular ethylbenzene and p/m-xylenes, were also found during the measurement campaign period. Because of their anthropogenic origin, an evaluation of air masses was performed in our study by using the HYSPLIT transport and dispersion model from NOAA Air Resources Laboratory [112]. Results revealed the long-range transportation from cities with significant anthropogenic activities, such as Tampere. This observation increased the potential applications of the developed NTME-GC-MS method.

Dimethylamine (DMA) was also tentatively identified in this study, because of its likely involvement in atmospheric nucleation [113]. However, even though characteristic ions and similar retention time as for the corresponding standard were observed, DMA was not studied further due to its almost no retention in the column and the possible chromatographic overlapping and/or interference caused by ethylamine and/or CO_2.

Although several compounds were successfully collected and measured, the development of a calibration method would have been helpful to make the final conclusions in this work. It would have enabled to provide not only atmospheric concentrations but also more information about the influence of the adsorbent type (microporous/mesoporous, mechanical/thermal stability) and sampling conditions (temperature, sample flow during adsorption) on the breakthrough volumes and their consequent effect on the efficiency and reproducibility of collection. For proper calibration, gaseous standards of target analytes and representative internal standards at known concentrations are required, and breakthrough volumes must be determined for all the referred compounds under the worst-case scenario atmospheric conditions influencing NTME collection.

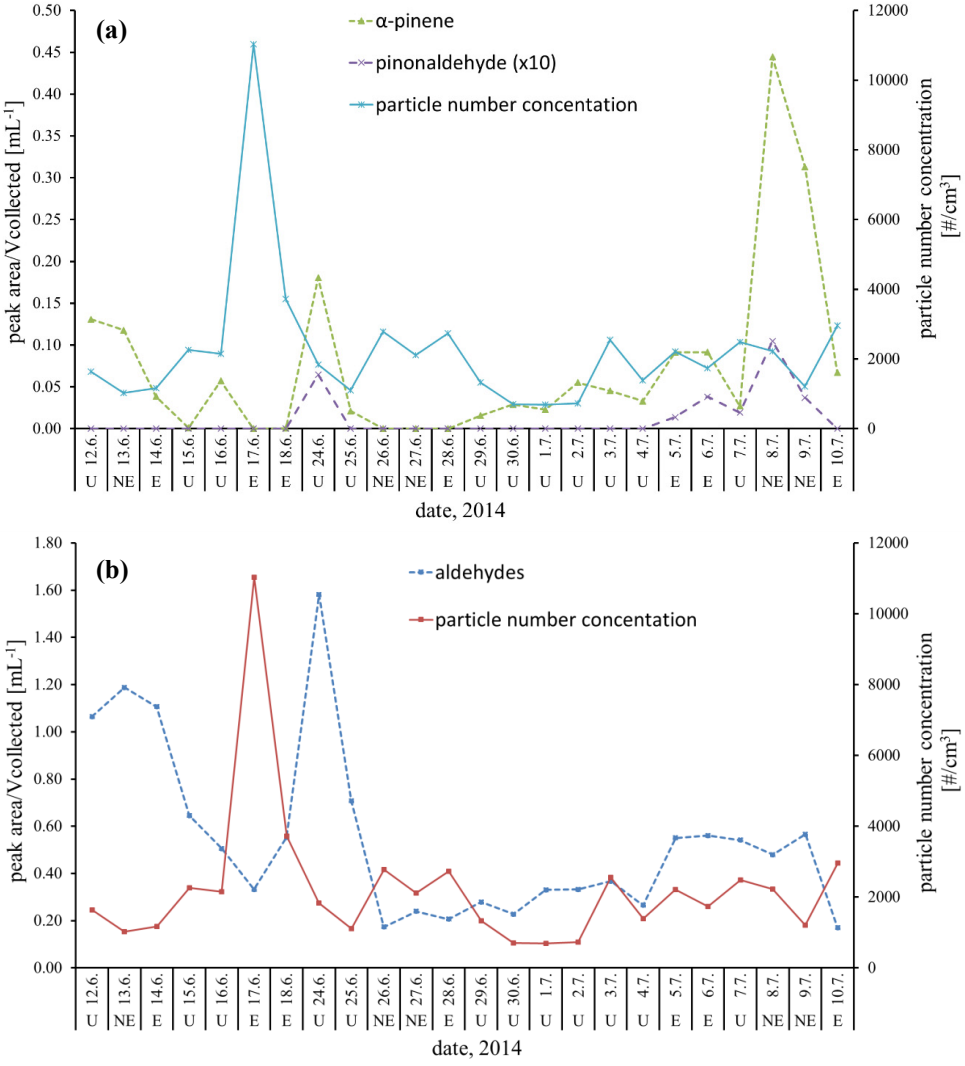

Figure 19. *Comparison between the particle number concentration (#.cm^{-3}) and the daily average amounts (peak areas/Vcollected) of α-pinene and pinonaldehyde (a), and the sum of aldehydes (benzaldehyde, hexanal, heptanal, octanal, nonanal, and decanal) (b) collected by NTME and analysed by portable GC-MS in mid-summer 2014. (E. corresponds to a day when a nucleation event was observed, U. to an undefined event and NE. to a day without nucleation events) (Paper II).*

4.3 Measurement of atmospheric variations of biogenic volatile organic compounds during a snow melt event

The method developed in Paper II was applied to study the occurrence of variations on atmospheric BVOC amounts during a snow melt event. As can be seen from Fig. 20 A, the measured amounts of monoterpenes were smaller before the snow melt event when the temperature was higher and increased substantially after the melting of the snow when temperatures remained comparatively lower.

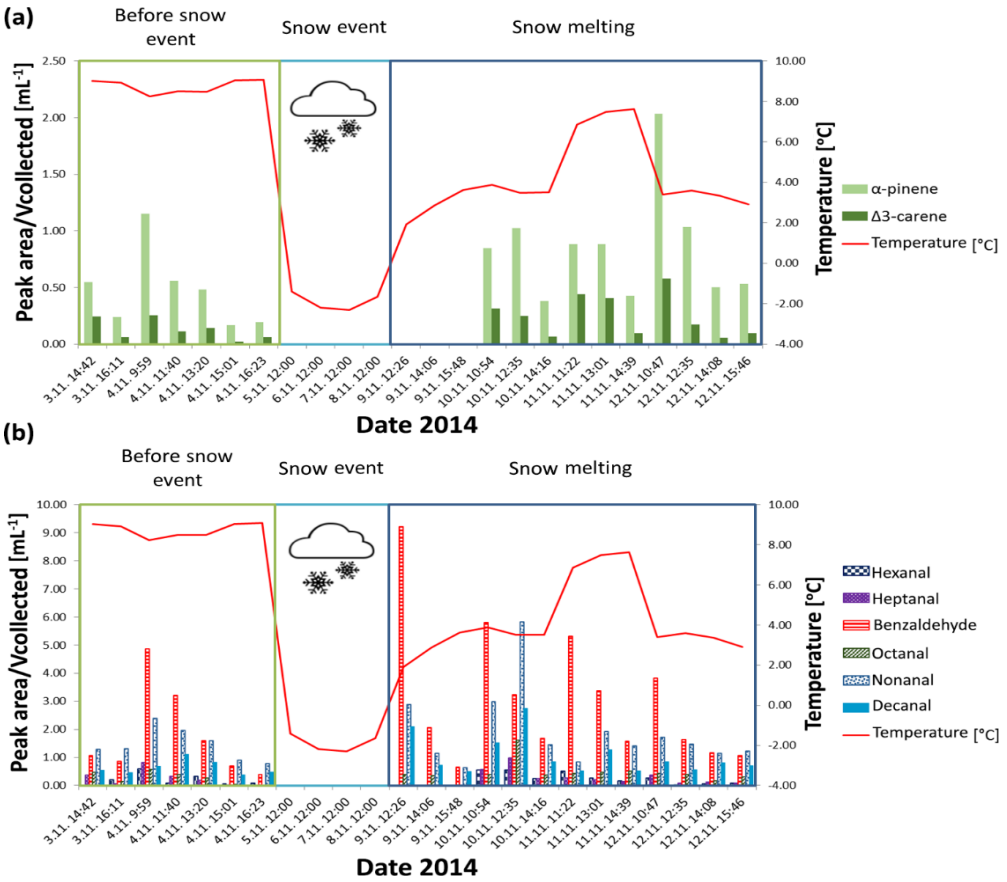

Figure 20. *Observation of an increase in monoterpene (a) and aldehyde (b) atmospheric amounts after a snow melt event in November 2014 (daily average temperatures were used on days when sampling was not performed) (Paper II).*

Monoterpene emissions at the studied boreal forest site in late autumn are mainly driven by temperature and therefore the observation of higher emissions before the snow melt event was expectable. This phenomenon suggests the occurrence of an accumulation of these compounds under or into the snow pack, and their subsequent release into the atmosphere after the melting of the snow. It can then influence atmospheric photochemistry, especially in spring after a long period of accumulation and retention of these compounds in the snow pack. Similar results were seen for aldehydes (Fig. 20 B), implying that these BVOCs also undergo a snow pack accumulation and can influence atmospheric processes after being subsequently released into the atmosphere when snow is melted. An accumulation of monoterpenes below and inside the snow pack has also been suggested in another study performed at the same sampling site [114]. Furthermore, an increase of nitrogen-containing compounds in aerosol particles at snow melt has been observed [115].

However, other factors can as well contribute to the observed results. Increased soil moisture and temperature enhances the soil microbial activity, including leaf litter decomposition, which lead to higher monoterpene emissions [116-118]. Furthermore, emission bursts after precipitation events have been observed previously [119] and attributed primarily to surface adhesion disruption. This mechanism could also play a role in increased atmospheric VOC concentrations.

4.4 Characterization of plant and soil volatiles from the boreal forest floor and understory

BVOC fluxes from boreal forest tree canopies have been the most intensively studied in the past years. However, forest floor emissions can also contribute significantly to the total BVOC budget at this ecosystem and, due to the high reactivity of BVOCs, they are likely to influence atmospheric chemistry below the canopy [99, 120, 121]. Forest floor fluxes consist of emissions from vegetation and soil and are influenced by both biological processes and physical environmental factors [99]. Generally, BVOC emissions from soil to the atmosphere are 1-2 orders of magnitude lower than those from aboveground vegetation [120].

Understory level BVOC measurements are scarce and have been mostly performed by PTR-MS that cannot separate species with the same nominal mass [99, 122]. In Paper III, the measurement of understory emitted BVOCs was performed from soil chambers by static SPME and portable GC-MS. The type and relative amounts of measured BVOCs were subsequently compared with those obtained from ambient air samples collected simultaneously at understory level by dynamic SPME and measured with the same analytical instrumental system. The influence of external sources on the performed measurements was also evaluated in this study.

Static SPME sampling was chosen because it does not require any additional equipment, such as pumps and/or sampling devices, and it granted more flexibility for sampling from

different chambers. The needle could then be easily inserted from a small hole into the closed chamber and the sorbent material exposed to the understory air. A proper air mixing was also provided by fans installed inside the chambers, which improved the mass transfer from the air to the fiber sorbent. Understory levels were assumed to be sufficiently high due to the pre-concentration of analytes in the chambers after their closure. For ambient air sampling, dynamic SPME was employed to ensure the collection of sufficient mass of analyte, by improving mass transfer processes, and because VOCs extraction on the fiber sorbent is increased with an increase in wind velocity from 0 to 5 cm/s as has been reported previously [56].

Several fibers were initially tested in the laboratory to select the one with the best performance for the described study. As seen in Fig. 21, PDMS/DVB and PDMS/DVB/CAR fibers gave the best extraction efficiencies for the most abundant BVOCs at the studied boreal forest site. Even though the extraction efficiency of PDMS/DVB/CAR was slightly better than that of PDMS/DVB, the latter was chosen due to a previously reported study where competitive adsorption of isoprenoids was noticeable inferior for PDMS/DVB when compared to PDMS/DVB/CAR [123].

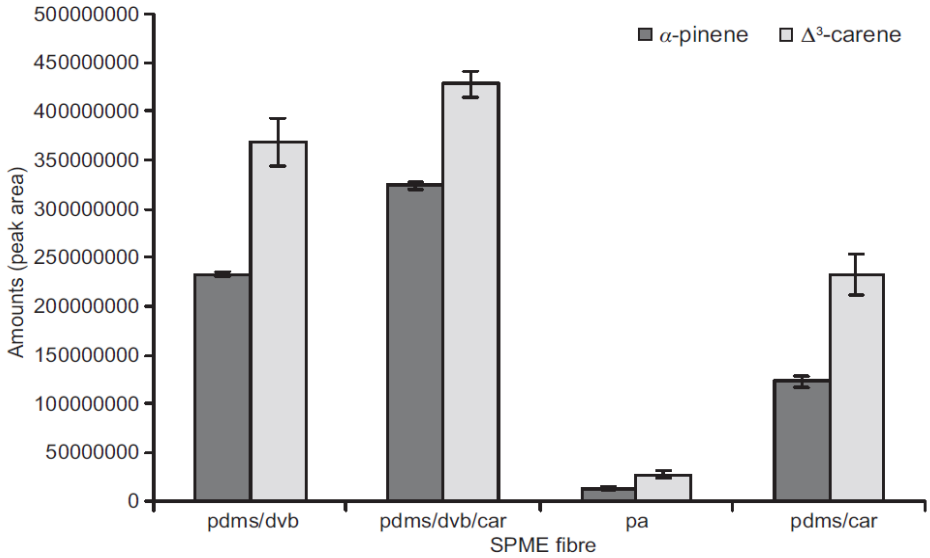

Figure 21. *Extraction efficiency ± SD of α-pinene and Δ³-carene using different SPME fibre materials (PDMS/DVB, PDMS/DVB/CAR, PA and PDMS/CAR) (Paper III).*

The fiber-to-fiber variability of SPME was a concern during this study, because there was a need to use simultaneously several SPME fibers for comparison purposes. Hence, the reproducibility was studied by exposing three different SPME fibers with the same material to the ambient air. The extraction efficiencies of these fibers were compared and the experiment was repeated twice. The obtained relative standard deviations were 9% and 12% for α-pinene and of 26% and 15% for Δ^3-carene. These RSD values appear to be

satisfactory considering the inherent fiber-to-fiber variability of SPME and the fact that the measured analytes are present in the atmosphere at trace amounts [124, 125]. The fiber-to-fiber variability was also evaluated during the whole campaign by collecting simultaneously two SPME samples from a soil chamber and from ambient air. As demonstrated in Figs. 22-24, for most of the measurements the variability was good enough to distinguish the different amounts of analytes in distinct soil chambers (see further discussion). The occasional deviations observed between repetitive measurements within this campaign may reflect some inconsistency in the manual sampling/injection processes.

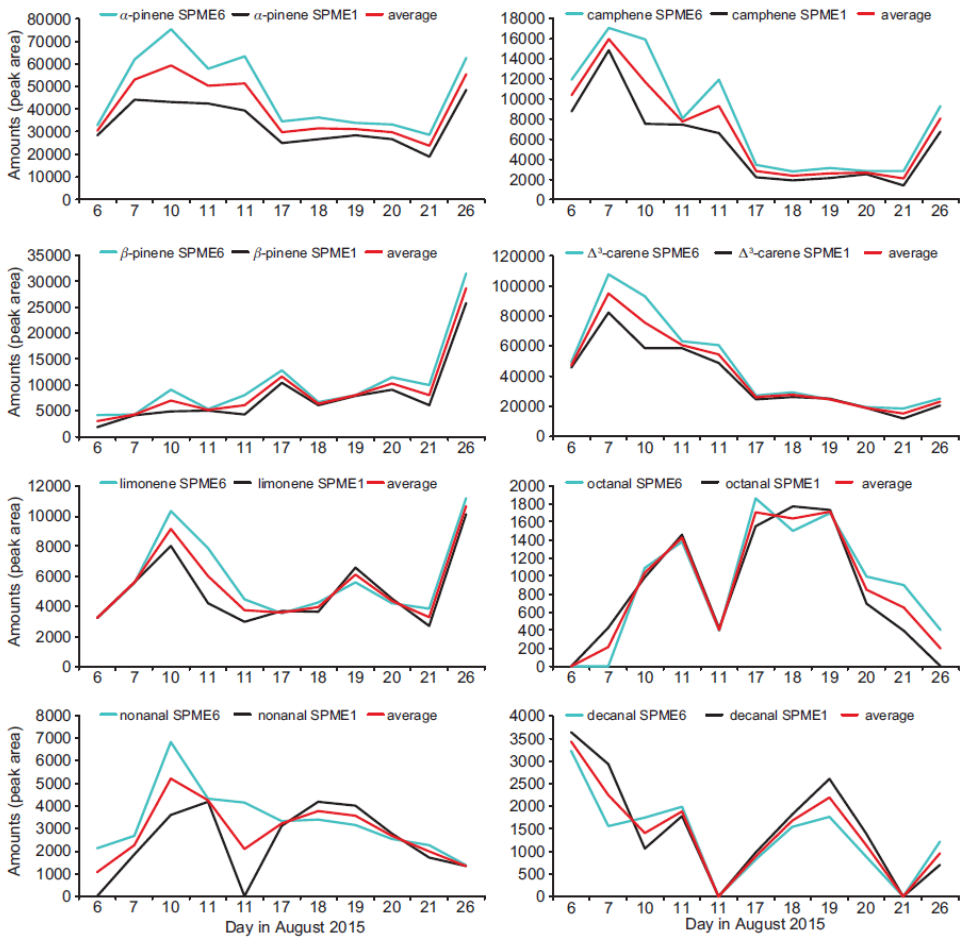

Figure 22. *Extraction of monoterpenes and aldehydes from a soil chamber on two different SPME fibers during the whole campaign period. Samples were analysed by portable GC-MS (Paper III).*

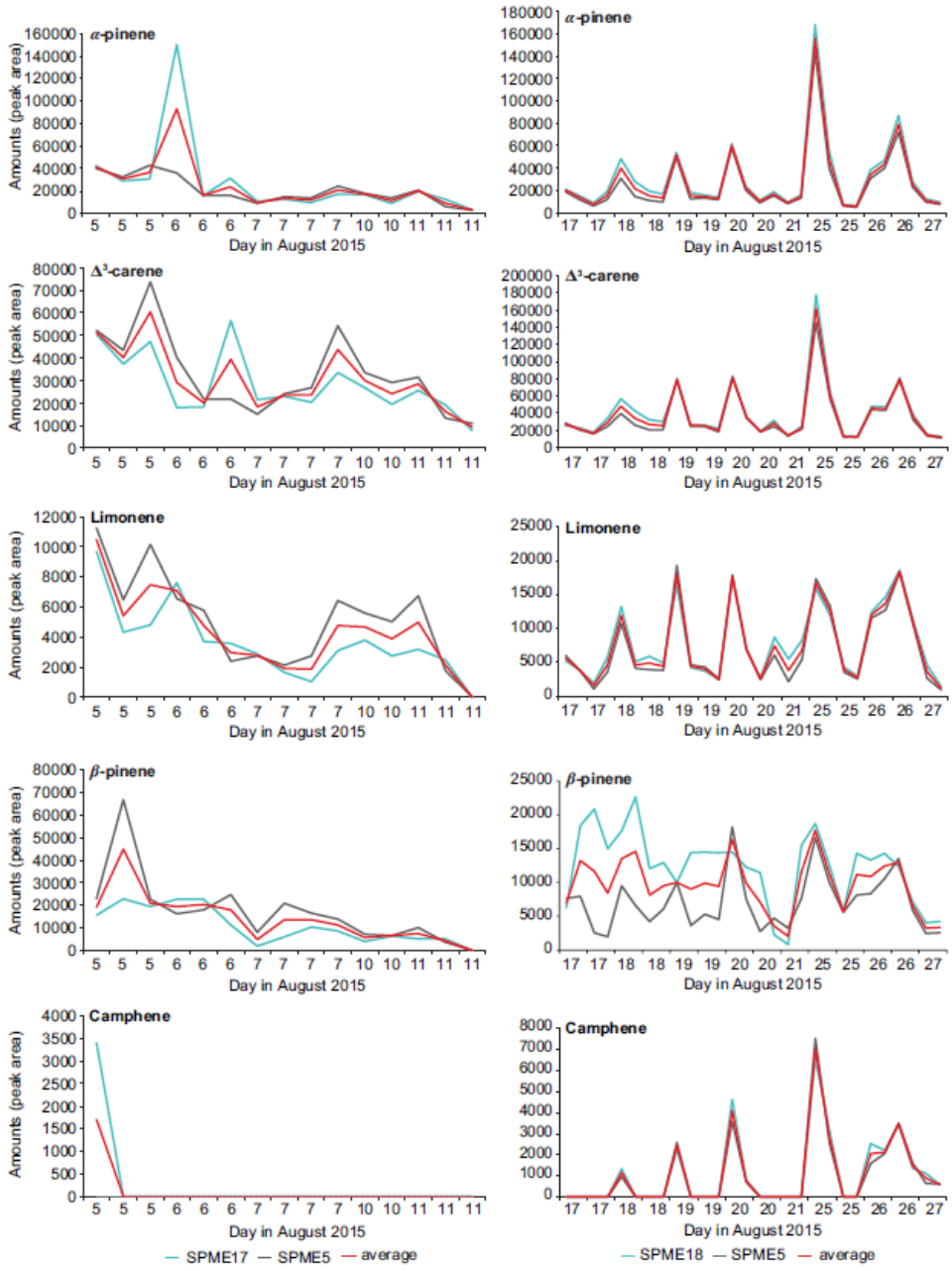

Figure 23. *Dynamic extraction of monoterpenes from ambient air on two different SPME fibers during the whole campaign period. Samples were analysed by portable GC-MS (Paper III).*

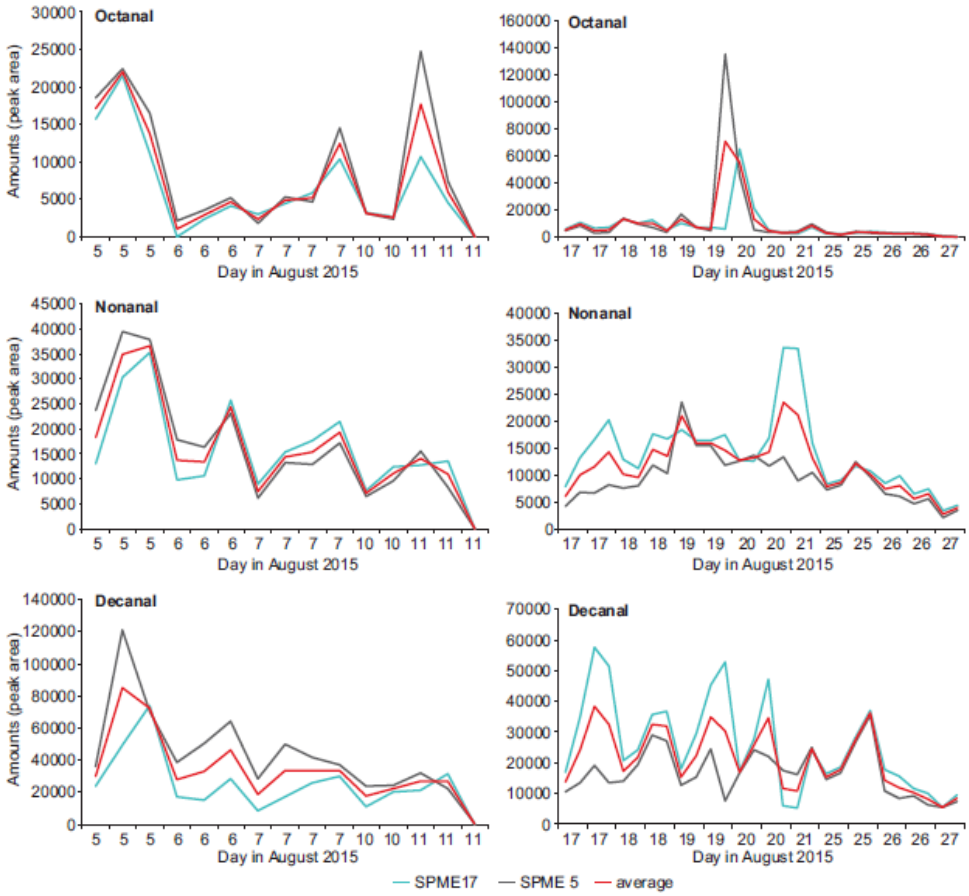

Figure 24. *Dynamic extraction of aldehydes from ambient air on two different SPME fibers during the whole campaign period. Samples were analysed by portable GC-MS (Paper III).*

Another parameter optimized during method development was the extraction time, which was 40 minutes for the static collection from chambers and 60 minutes for the dynamic ambient air sampling. The portable GC-MS analysis was validated before the measurement campaign by collecting passively samples with two SPME syringes from the same chambers, followed by their analysis by both portable and conventional GC-MS (Fig. 25). A good agreement was observed between these two systems. Dynamic SPME collection was validated in Paper I by comparison with PTR-MS measurements.

The characterization of the most abundant BVOCs in soil chambers and in ambient air was subsequently performed. Five different monoterpene species were successfully separated and tentatively identified, including α-pinene, camphene, β-pinene, Δ^3-carene and limonene (Fig. 26). α-Pinene and Δ^3-carene dominated understory level emissions in the three studied chambers and in ambient air. The highest amounts were measured in chamber no. 10, while the other two chambers had similar emission profiles with slightly higher

fluxes in chamber no. 13. Results demonstrated that the type and relative amounts of monoterpenes are similar inside and outside the chambers at understory level, even though the vegetation species, vascular plant coverage and analyte fluxes were clearly different.

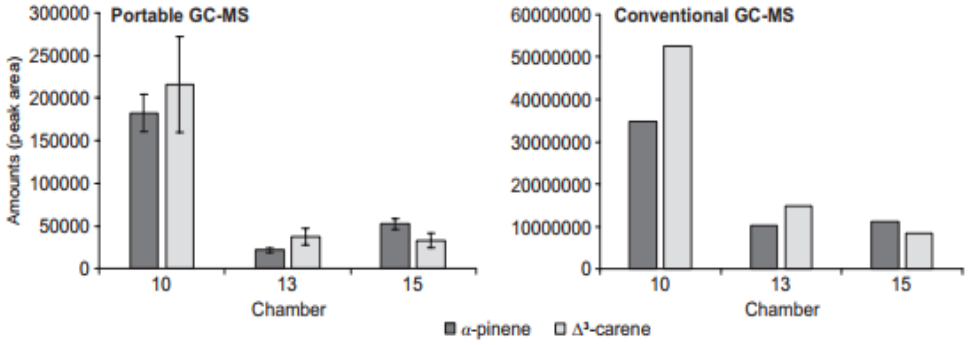

Figure 25. *Comparison between amounts of α-pinene and Δ³-carene collected by SPME and measured simultaneously from three different soil chambers by portable and conventional GC-MS. Error bars are the highest standard deviations obtained in the reproducibility experiment (Paper III).*

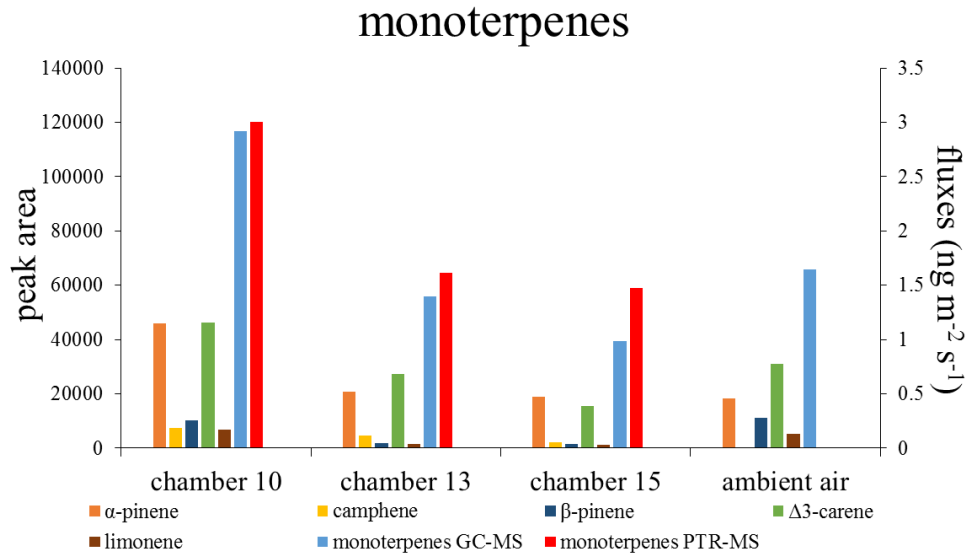

Figure 26. *Average amounts (peak area, primary axis) of monoterpenes measured during the sampling campaign by portable GC-MS. Samples were collected by static SPME from soil chambers and by dynamic SPME from ambient air. Monoterpene fluxes (ng m^{-2} s^{-1}, secondary axis) measured in the soil chambers by PTR-QMS are shown for comparison (Paper III).*

A similar trend was also observed for the sum of monoterpenes collected from the same soil chambers and measured by portable GC-MS and the PTR-QMS monoterpene flux measurements, thus confirming the reliability of the system used. Even though these amounts are not truly comparable because concentrations and fluxes are different units of measurement, an increase in emissions will naturally result in higher concentrations inside the chamber.

When the measured amounts from soil chambers were compared with those from ambient air, a similar temporal trend was observed for monoterpenes during the whole sampling period (Fig. 27), suggesting that the same environmental factors (e.g. temperature) influence BVOCs emissions from the higher plants and understory.

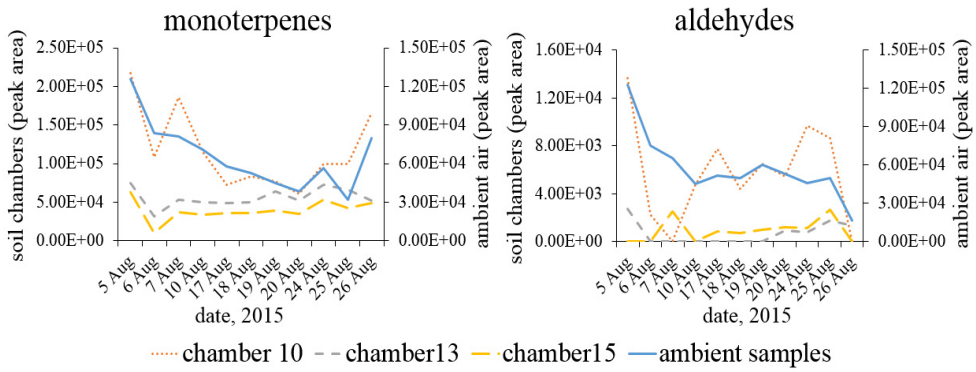

Figure 27. *Comparison between the amounts of monoterpenes and aldehydes measured in soil chambers and in ambient air by SPME-GC-MS (Paper III).*

The type and relative amounts of aldehydes in soil chambers and in ambient air were also evaluated. Three different aliphatic aldehydes were found in both media, namely octanal, nonanal and decanal. As seen from Fig. 27, soil chamber emissions seemed to be substantially lower when compared to the amounts measured in ambient air. This suggests that the main source of studied aldehydes is not the soil nor understory vegetation, or that soil/understory are acting as a sink for these carbonyl compounds. However, quantitative studies are still needed to confirm this conclusion.

A temperature-dependence of monoterpene emissions was observed in the measurements from soil chambers performed in this study. Oppositely, photosynthetic active radiation (PAR) did not have any visible effect on the amounts of measured monoterpenes, agreeing with emissions resulting from the temperature-dependent residence in specific storage structures located internal or external to the leaf [29, 109]. However, in ambient studies, light and temperature parameters are correlated and any conclusion related to their effect is challenging without additional laboratory studies and/or the use of other techniques (e.g. $^{13}CO_2$ labelling).

The effect of wind speed and wind direction on the measured amounts of BVOCs was also evaluated. Higher amounts of BVOCs were measured when wind speed decreased, which is a result of the accumulation of these compounds closer to the sources due to reduced mixing. As of particular interest, the impact of wind direction was evaluated to indicate the influence of the surroundings on the sampling site. The results proved that the amounts of monoterpenes were significantly higher when wind was from south-east, which coincides with the presence of two sawmills located 6.3 km south-east from the sampling site (Fig. 28). Additionally, the influence of different tree chemotypes, so called pinene or carene trees, on the surrounding forest can also impact on the measurement amounts of terpenoid compounds [103].

The effect of wind direction seemed to be substantial and must be taken into consideration when measurements are performed at the sampling site. More studies are also required to characterize surrounding emissions and to increase understanding of their influence on the physical chemistry of the ecosystem.

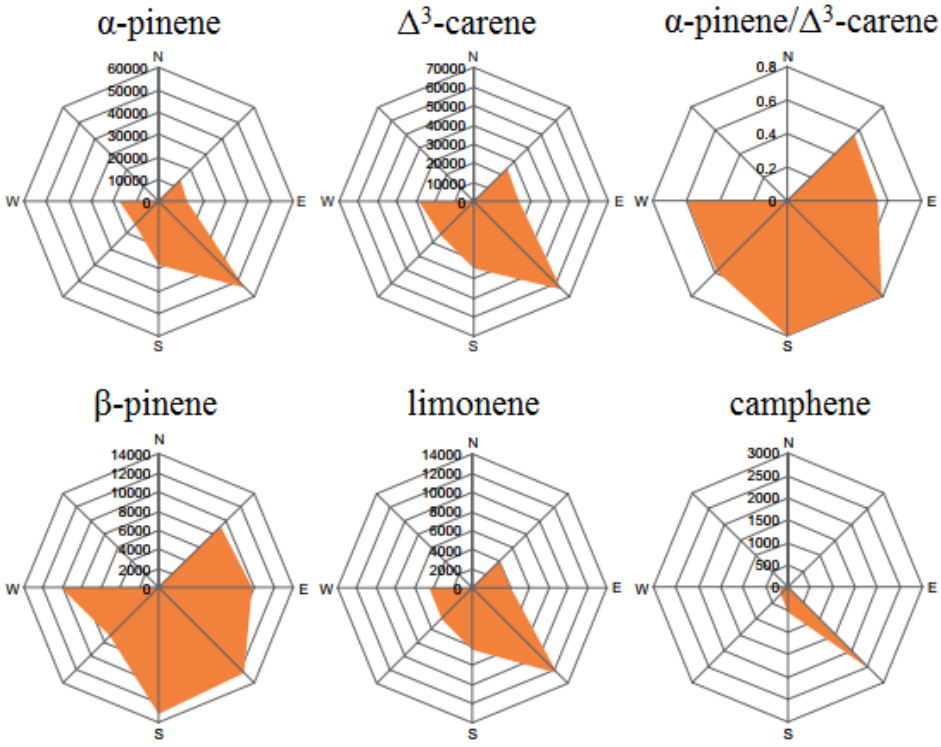

Figure 28. *Influence of the wind direction (measured at 33.6 m height) on the observed amounts (peak area) of α-pinene and Δ^3-carene (Paper III).*

4.5 Field sampling of volatile organics using solid-phase microextraction Arrow

A novel SPME Arrow sampling system was also employed for the measurement of BVOCs in the atmosphere (Paper IV). This system offers higher sample capacity with the same advantages of the most conventional SPME fibers, including the compatibility for direct thermal desorption in a conventional GC-MS [63]. These characteristics are important for field applications due to the trace levels of BVOCs (few pbbv to pptv or less) commonly present in forest air, which usually require significant pre-concentration to obtain measurable amounts of analyte.

The study combined laboratory experiments and field measurements for the better understanding of the SPME Arrow sampling system. The laboratory studies consisted of the determination of extraction profiles, a comparison between different SPME-based techniques, sampling modes (static vs dynamic) and sorbents (PDMS/DVB vs PDMS/Carbon WR), and an assessment of the impact of temperature and relative humidity on the collection efficiency. The study was performed for two representative monoterpenes (α-pinene and Δ^3-carene) and aldehydes (octanal and decanal), which have constituted a significant fraction of the total measured compounds in our previous studies (Paper I-III). Field measurements were performed for the same comparison purposes and to evaluate the effect of meteorological parameters (temperature, relative humidity, precipitation, ozone and PAR) and PNC on the measured amounts of BVOCs under atmospherically relevant conditions.

In the laboratory experiments, extraction profiles demonstrated the different kinetics for both sorbents and SPME-based techniques used. The kinetics of extraction was faster for SPME Arrow than for SPME fiber and for PDMS/Carbon WR sorbent in comparison to PDMS/DVB (Fig. 29). These results show that SPME Arrow is seemingly more efficient than SPME fiber due to a more rapid extraction and consequent enhancement of analyte collection. A faster extraction was also noticeable when dynamic extraction was used (Fig. 30). Monoterpenes reached equilibrium faster than aldehydes that did not equilibrate during the experimental time.

Extraction efficiencies for the different SPME-based techniques and sorbent materials were further studied. As seen from Fig. 31, SPME Arrow increased the extraction efficiency by about two times when using PDMS/DVB and three times with PDMS/Carbon WR when compared to conventional SPME fibers. The materials demonstrated compound specific extraction efficiencies, with both materials adsorbing more Δ^3-carene than α-pinene. With regard to aldehydes, differences in extraction efficiencies between the two referred materials were not statistically relevant.

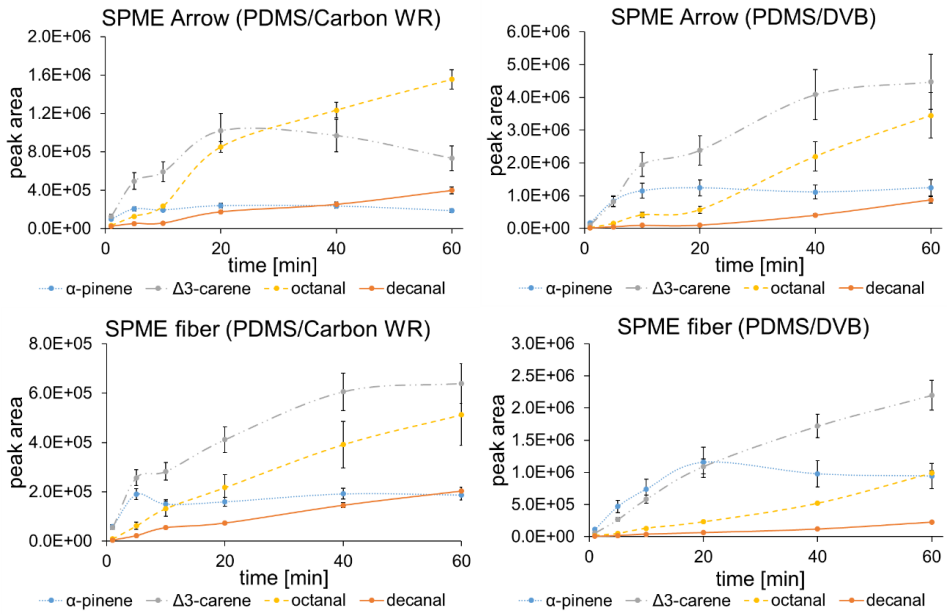

Figure 29. *Extraction time profiles obtained for the studied analytes using SPME fiber and SPME Arrow coated with PDMS/Carbon WR and PDMS/DVB (Paper IV).*

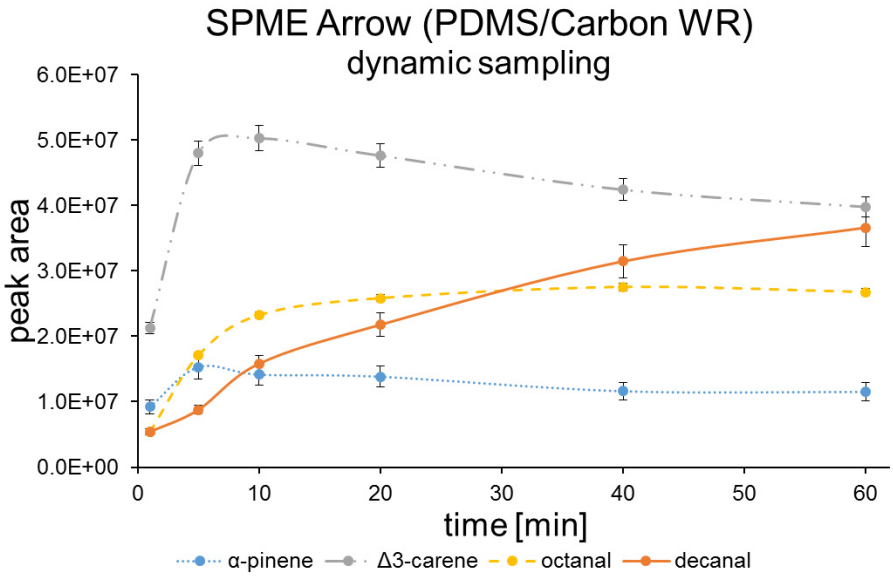

Figure 30. *Extraction time profiles obtained for the studied analytes using dynamic sampling by SPME Arrow coated with PDMS/Carbon WR (Paper IV).*

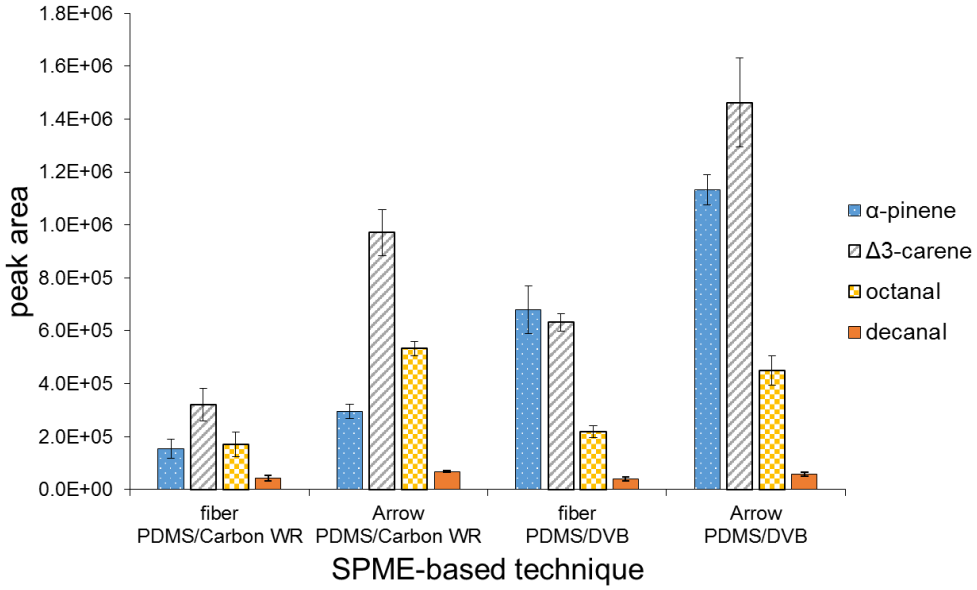

Figure 31. *Comparison of the extraction efficiencies obtained with SPME Arrow and SPME fiber coated with PDMS/Carbon WR and PDMS/DVB (Paper IV).*

When static and dynamic samplings were compared (Fig. 32), extraction efficiencies with both systems were similar when equilibrium was reached as was the case for α-pinene. However, prior to equilibrium, extraction efficiencies were higher for dynamic sampling due to the previously described faster kinetics of extraction.

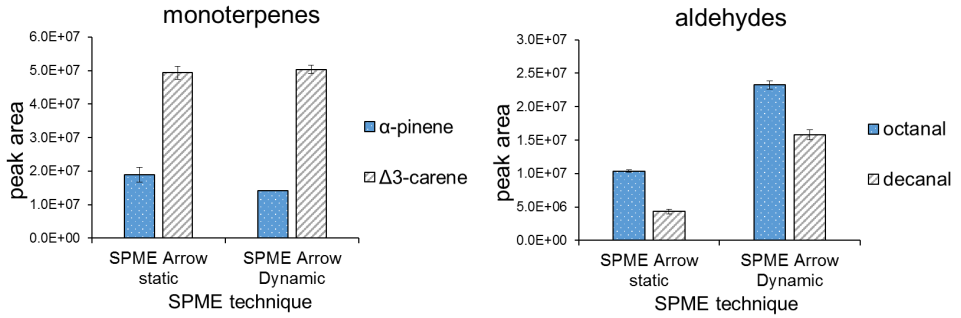

Figure 32. *Comparison between static and dynamic sampling by SPME Arrow (PDMS/Carbon WR) (Paper IV).*

The negative effects of temperature and relative humidity on SPME fiber collection efficiency have been reported previously [126] and a similar impact was expected when using SPME Arrow. As can be seen from Fig. 33, an increase of 10 °C resulted in a decrease of the extracted amounts of monoterpenes for both SPME Arrow sorbents. However, the effect was much more prominent for PDMS/Carbon WR than for PDMS/DVB and for α-

pinene than for Δ^3-carene. The same result was obtained for SPME fibers, as described in Paper IV. Furthermore, a similar decrease has been observed in another study where monoterpenes (α-pinene and β-pinene) were collected at different temperatures with a PDMS/DVB fiber and analyzed by GC-MS [127]. In the referred study, an increase in temperature from 23-36 °C resulted in a decrease in the concentration of α-pinene by approximately 35%, while in our results the decrease with the same type of SPME fiber was about 25% for α-pinene when temperature was increased from 10 to 20 °C. In the same study, the effect of temperature has also been tested for sesquiterpenes and no effect was observed. This observation is also consistent with our results where compounds with lower volatility evidenced less or no temperature effects compared to the more volatile ones.

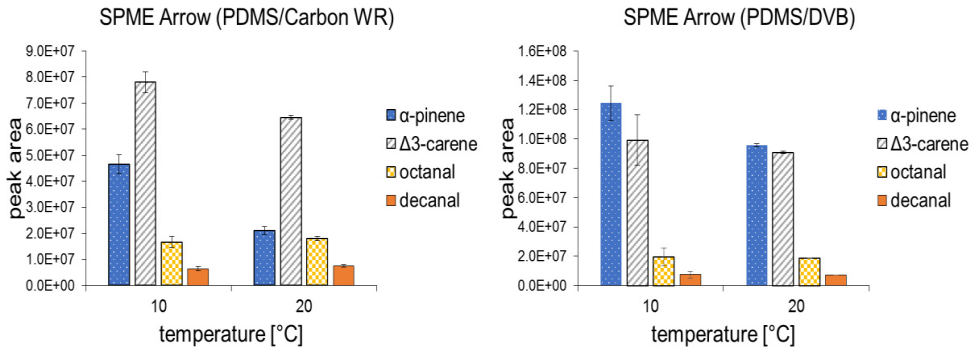

Figure 33. *Effect of temperature (°C) on the extraction efficiencies of SPME Arrow coated with PDMS/Carbon WR and PDMS/DVB (Paper IV).*

On the other hand, an increase in humidity from 40 % to 80 % did not change significantly the extraction of studied BVOCs and therefore should not have a high impact on the performance of collection during field measurements. The small effect of relative humidity when using hydrophobic materials has been also observed previously for the collection of α-pinene and limonene with a PDMS fiber [126]. For that reason, any observed effect of humidity on the measured amounts of BVOCs is probably related to the impact of this parameter on the dynamics of biosphere-atmosphere relations, such as sink/source effects.

The field measurements supported the results achieved under laboratory experimental conditions. As observed in Fig. 34, SPME Arrow improved significantly the collection efficiency for the studied analytes. Extraction enhancement was about two times for monoterpenes and seven to eight times for aldehydes. This enhancement proves the potential of SPME Arrow for the measurement of species present at very low concentration in the atmosphere.

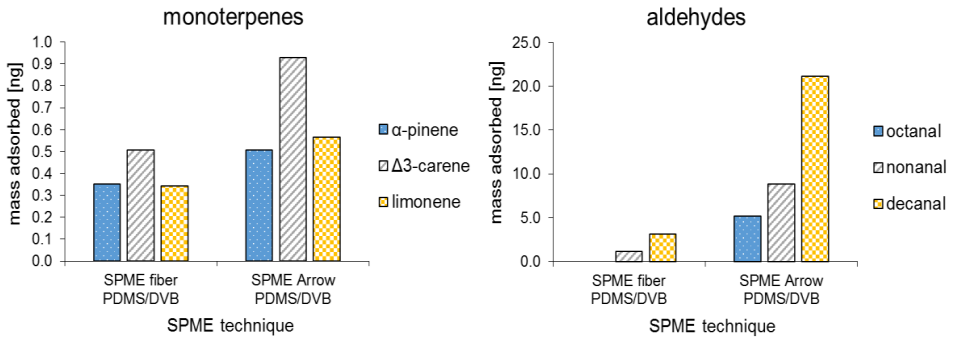

Figure 34. *Comparison between the mass of identified monoterpenes (α-pinene, Δ^3-carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with different PDMS/DVB SPME devices (fiber and Arrow) from ambient air and measured by GC-MS (Paper IV).*

Interestingly, high levels of limonene were measured with both materials used (Fig. 35). This result has not been observed in previous measurements performed at the SMEAR II station that indicated a clear dominance of α-pinene and Δ^3-carene over the remaining monoterpenes [128]. Hence, it is very likely that these materials have a higher affinity towards limonene compared to the dominant monoterpenes. The selectivity of materials used in SPME can be an advantage compared to other techniques requiring long sampling times for the collection of detectable amounts of BVOCs. A calibration of SPME would correct the differences in extraction efficiencies for quantitative analysis. However, isomerization at the surface of the extraction material might also cause an increase in the measured amounts of limonene and an evaluation of this phenomenon is required.

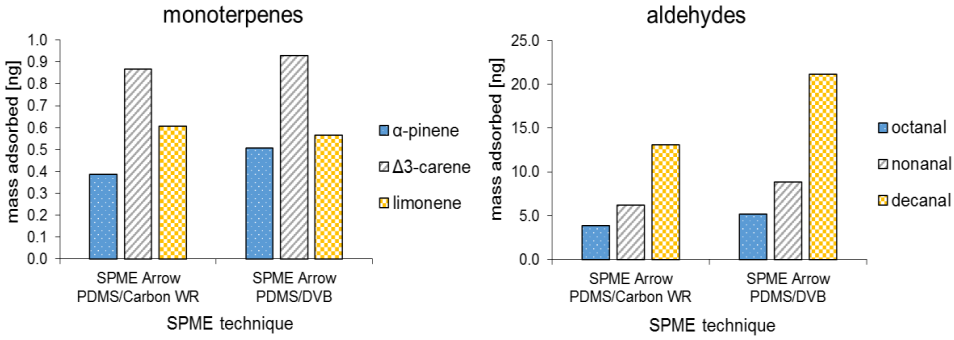

Figure 35. *Comparison between the mass of identified monoterpenes (α-pinene, Δ^3-carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with different SPME Arrow sorbents (PMDS/DVB and PDMS/Carbon WR) from ambient air and measured by GC-MS (Paper IV).*

The comparison between static and dynamic SPME Arrow collection was also performed in the field and a slight improvement on the extraction efficiencies was observed for all the analytes with a dynamic sampling mode (Fig. 36). However, the differences were relatively small, suggesting the proximity to or the attainment of the equilibrium state where an increase in the time of extraction does not result in higher amounts of analyte extracted on the SPME materials. A possible reason for this evidence is that during field measurements wind increased the mass transfer from the air to the sorbent in a similar way as to the sampling devices used for dynamic extraction. An exception was observed for limonene for which a significant increase was still observed with the dynamic sampling. A possible reason for this evidence is that limonene requires longer sampling times to reach equilibrium. The non-attainment of equilibrium would cause noticeable differences in the extraction amounts measured with static and dynamic collection due to unequal wind velocity and flow rate of the dynamic sampling device.

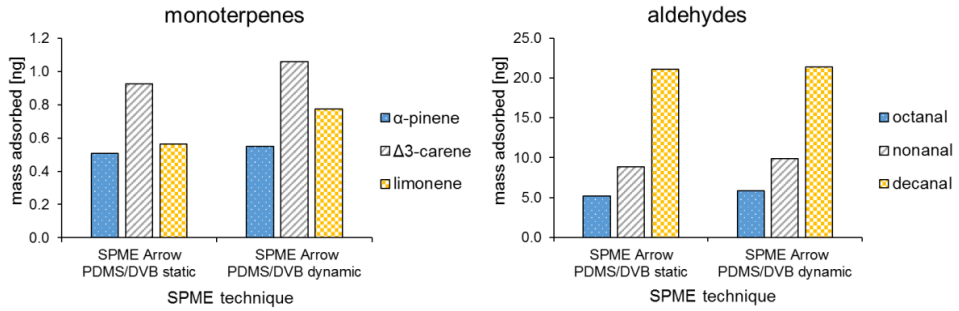

Figure 36. *Comparison between the mass of identified monoterpenes (α-pinene, Δ^3-carene and limonene) and aldehydes (octanal, nonanal and decanal) collected with different sampling modes (static and dynamic) by SPME Arrow from ambient air and measured by GC-MS (Paper IV).*

Meteorological parameters are of particular concern during SPME sampling due to their potential influence on the collection efficiency. Temperature has two opposing effects during field sampling. A temperature increase enhances VOC emissions from Scots pine, but because adsorption is an exothermic process it will also reduce the distribution constant of the analytes [55, 109]. As represented in Fig. 37, the amounts of monoterpenes followed the trend of temperature during most of the time. However, temperature remained almost constant during the entire campaign and for that reason it was not expected to be the major factor contributing to changes in monoterpene concentrations.

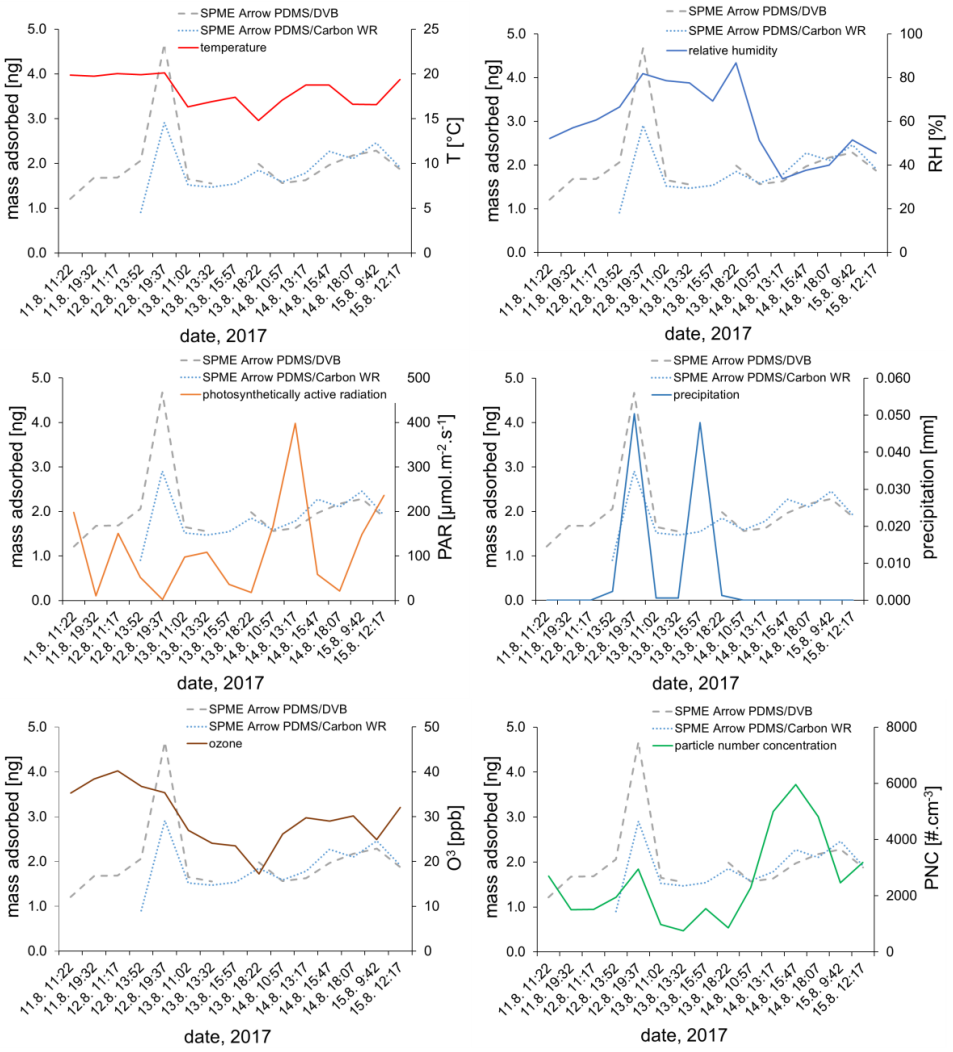

Figure 37. *Effect of temperature (°C), relative humidity (%), photosynthetically active radiation (µmol.m^{-2}.s^{-1}), precipitation (mm), ozone (ppb), and particle number concentration (#.cm^{-3}) on the mass of monoterpenes adsorbed on the SPME Arrows used in this study (PDMS/DVB and PDMS/Carbon WR) and measured by GC-MS (Paper IV).*

Interestingly, monoterpene amounts were increased with relative humidity and precipitation, which is consistent with previous measurements where monoterpene emissions were larger at high humidity during and after rain events [119]. In addition to humidity, ozone and PAR were the most significant meteorological parameters affecting the measured monoterpene amounts, a fact that was expected due to the constancy of temperature during the sampling campaign.

The PNC increased with the amounts of monoterpenes in the atmosphere, which is also expected since monoterpenes are precursors of several monoterpene oxidation products that can contribute to aerosol particle formation [129]. Furthermore, at days when PNC was extremely high, the amounts of monoterpenes in the atmosphere were low. This finding can be explained by the increased atmospheric photo-oxidation under favorable conditions for SOA formation.

The ratio between the amounts of monoterpenes sampled with PDMS/Carbon WR and PDMS/DVB decreased at high temperatures and humidity. These results were in line with the observations from the laboratory experiments, where a more pronounced decrease in adsorption was observed for PDMS/Carbon WR compared to PDMS/DVB when these parameters increased.

A similar evaluation of the effect of atmospheric conditions on the measured amounts of aldehydes was performed. As represented in Fig. 38, some trend between aldehyde amounts and temperature was also observed, which suggested the existence of a temperature-dependence on aldehyde emissions. However, as referred previously, the temperature remained almost constant during the sampling periods and more studies under controlled laboratory conditions are still required to confirm this observation. Relative humidity and precipitation seemed to influence negatively the amounts of aldehydes in the atmosphere, even though the effect was not seen when concentrations were high. This result can be explained by the fact that these compounds are dissolvable in water at low concentrations, but additional laboratory studies are needed to study in more detail the humidity influence on the measured amounts of aldehydes at different concentrations.

A correlation of aldehydes with ozone was verified, which was expected since ozone is known to increase aldehyde emissions from vegetation [34]. Interestingly, any significant correlation was observed between PAR or PNC and the measured amounts of aldehydes. This result suggests that the contribution of these compounds to atmospheric particle formation is smaller when compared to monoterpenes, probably due to their lower reactivity in the atmosphere [39]. However, because there is lack of laboratory experiments under controlled conditions, any conclusions about the effect of meteorological conditions cannot be drawn based only on field experiments. Furthermore, longer data sets are also required.

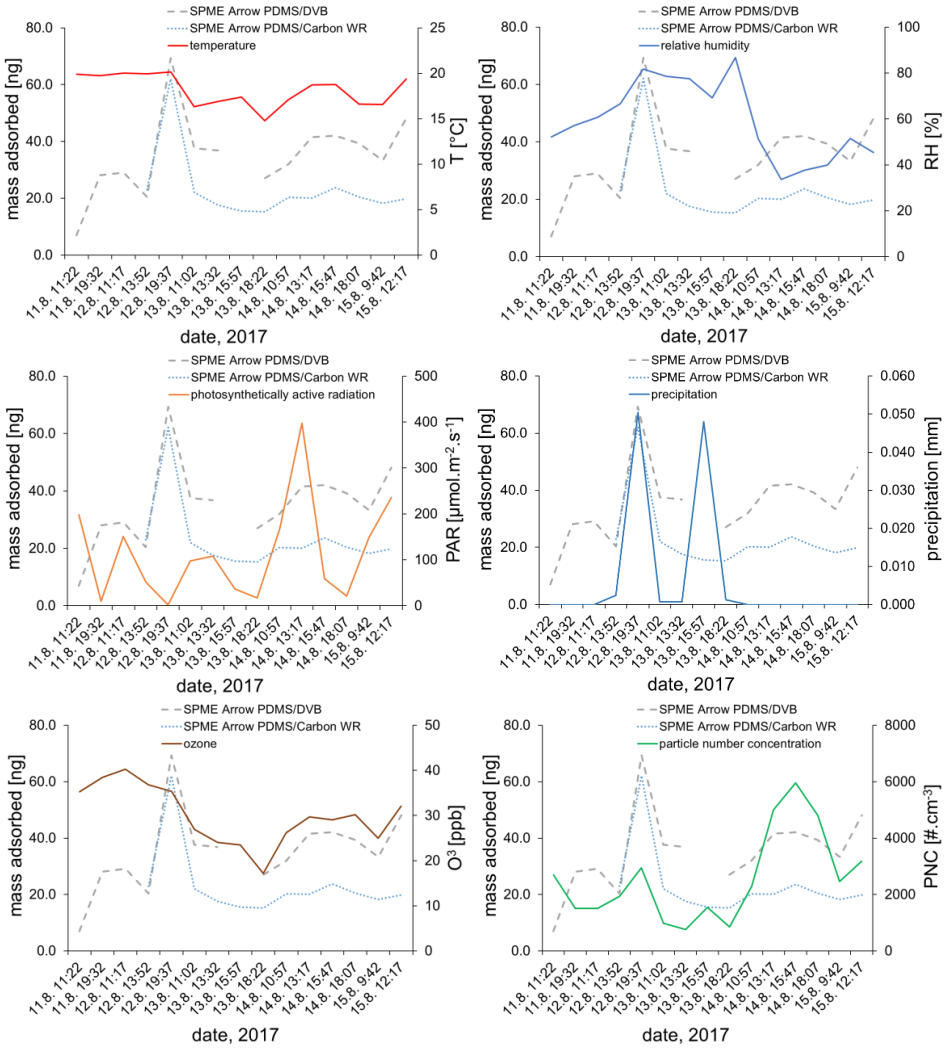

Figure 38. *Effect of temperature (°C), relative humidity (%), photosynthetically active radiation (µmol.m^{-2}.s^{-1}), precipitation (mm), ozone (ppb), and particle number concentration (#.cm^{-3}) on the mass of aldehydes adsorbed on the SPME Arrows used in this study (PDMS/DVB and PDMS/Carbon WR) and measured by GC-MS (Paper IV).*

5 Conclusions

The main aim of this doctoral thesis was to develop novel SPME-based analytical methods for the field measurement of BVOCs in the atmosphere. The SPME techniques used in this study included SPME fibers, NTME and SPME Arrow. The applicability of the developed methods were proved with field studies, such as the characterization of BVOC emissions from soil chambers.

The first developed method consisted of the combination of dynamic SPME collection with portable GC-MS. This method allowed fast on-site analysis of several biogenic organic compounds, including the main emitted monoterpenes and their oxidation products. Sample pre-treatment and long sampling lines were avoided, which reduced the risk of sample alteration during the analytical procedure. Due to the novel laboratory-made sampling system used for SPME, the kinetics of extraction was accelerated and the influence of wind speed on the SPME sorbent analyte extraction was reduced.

The exploitation of dynamic NTME combined with portable GC-MS for the field measurement of VOCs was also studied. This method enabled the identification and semi-quantitation of the most prevalent monoterpenes and aldehydes present at the boreal forest sampling site. Anthropogenic VOCs were also measured and their presence was related to a long-range transport after determining air mass origins. An accumulation of monoterpenes and aldehydes in the snow cover was observed with the developed method, a phenomenon that can have a considerable impact on atmospheric photochemistry and SOA formation and growth during spring-time when snow melts.

Monoterpenes sampled by SPME and measured by portable GC-MS at understory level played a major role in understory emissions and their relative concentrations were similar among all the used soil chambers and in ambient air. Aliphatic aldehydes were also measured at understory level. An assessment of the impact of surroundings on the measured BVOCs at the sampling site was performed and a marked contribution of emissions from nearby sawmills was ascertained.

Extraction efficiencies for the target analytes were significantly improved by using SPME Arrow compared to SPME fibers. A compound specific extraction was evidenced for both materials used (PDMS/DVB and PDMS/Carbon WR). Dynamic sampling was as well compared with static collection and only a minor improvement was observed during field measurements, indicating that wind affects the mass transfer processes from the air to the sorbent. The influence of temperature and relative humidity on the SPME collection was clarified in addition to that of meteorological conditions (temperature, RH, precipitation, PAR and ozone) and PNC on the measured amounts of BVOCs in the ambient air.

Altogether, these findings demonstrated the great potential of SPME-based methods developed in this study for the field measurement of atmospheric VOCs. The novel methodologies are more environmental friendly than conventional methods and provided

several advantages over those of other commonly used approaches. No sample preparation and storage are needed, nor long sampling lines and analysis times in addition to the capability for high pre-concentration. Furthermore, the associated portability allows the application of the different solid-phase microextraction based systems at practically anywhere without overwhelming infrastructure requirements. These advantages are particularly attractive for rapid screening. However, although several advances were achieved in this work, further development of calibration procedures for the methodologies utilized is still required due to the multiple sources of uncertainty during field measurements. Portable GC-MS instrumentation also demands more improvements, particularly with regard to sensitivity enhancement, higher selection of different columns and easier column change systems during laboratory/field procedures. Quantitative liquid analysis is also challenging due to the small dimensions of the portable GC liner.

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